Part 4. VB diagrams

VB diagrams by Shaik and Pross

- A powerful VB model for rationalizing reactivity :

J. Am. Chem. Soc. **1981**, *103*, 3692–3701

What Happens to Molecules as They React? A Valence Bond Approach to Reactivity

Sason S. Shaik

Contribution from the Department of Chemistry, Ben-Gurion University of the Negev, P.O.B. 653, Beer Sheva, 84120, Israel. *Received June 12, 1980*

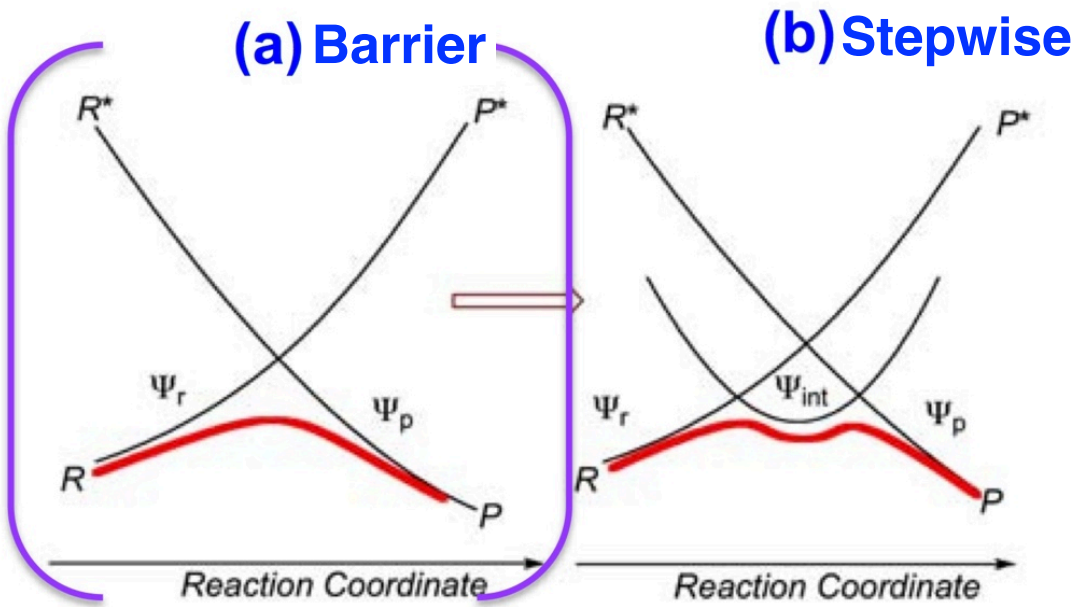
- Developed and applied since then to a huge number of organic chemical reactions, inorganic reactions, clusters and metalloenzymes

- Reviews : https://wiki.lct.jussieu.fr/workshop/index.php/VB_tutorial

VB diagrams by Shaik and Pross

- A powerful VB model for rationalizing reactivity :

Two archetypal diagrams that describe the major reactivity patterns in **any** chemical reaction :



Reminders

- Energy expressions from qualitative VB :

Energy of a determinant with *n pairs of interacting e⁻* : $\sigma 2n\beta S$

σ sign : + if attractive, – if repulsion

- **Bonding energy:**
- **Pauli Repulsion in VB Theory:**

Elementary Repulsion

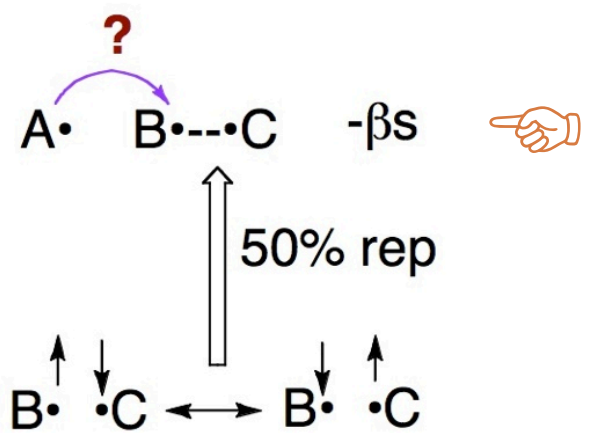
A: :B -4βs

A: •B -2βs

A• :B -2βs >0

A• —— •B E = 2βS <0

Nonbonded Interactions



Reminders

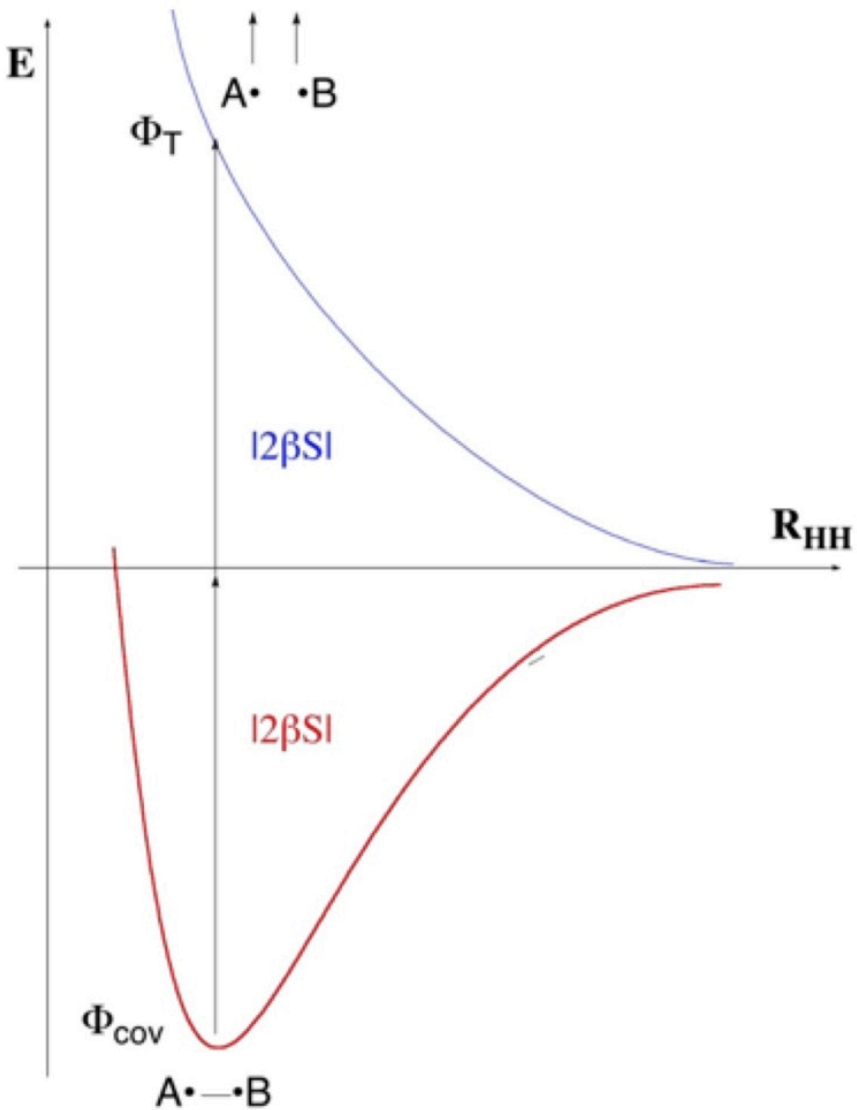
- Singlet-triplet gap :

- Lecture 1 :

$\Delta E_{ST} \approx 2De$

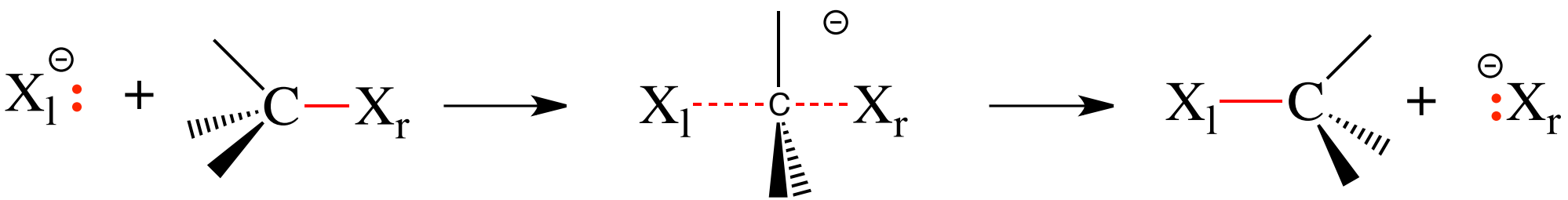
- A more accurate relation :

$$\frac{3}{4}\Delta E_{ST} \approx 2D_e$$



Principles

- VB diagram for the S_N2 reaction :



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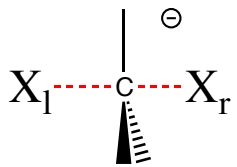
- VB diagram for the S_N2 reaction : 

$$\Psi_R \propto \left| x_l \overline{x_l} (c \overline{x_r} + x_r \overline{c}) \right|$$

$$\Psi_R = X:^- + (R_3C\bullet\text{–}\bullet X) \quad (+2\beta S)$$

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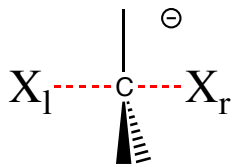

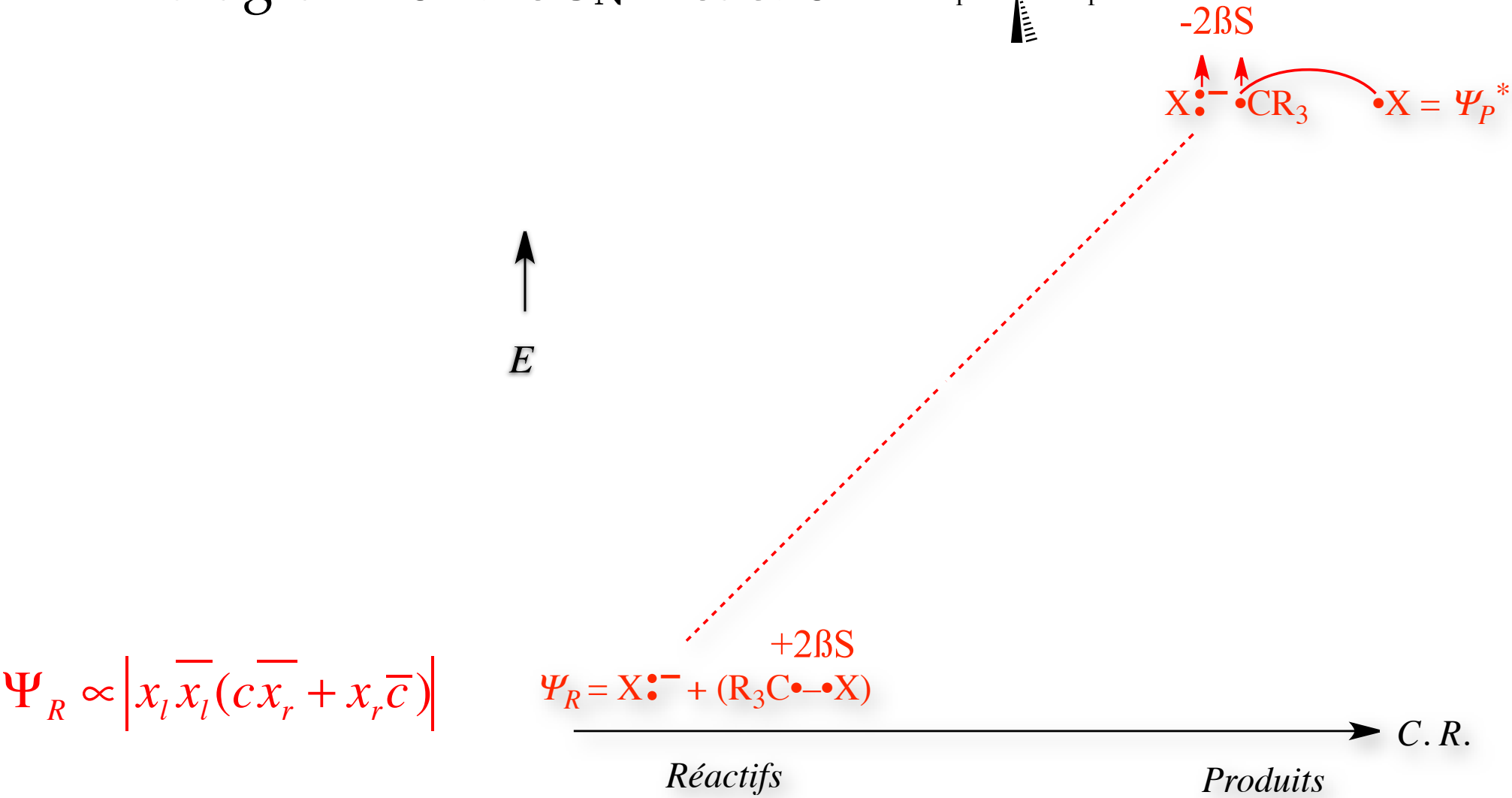

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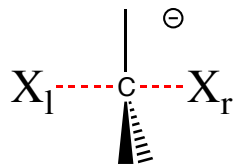

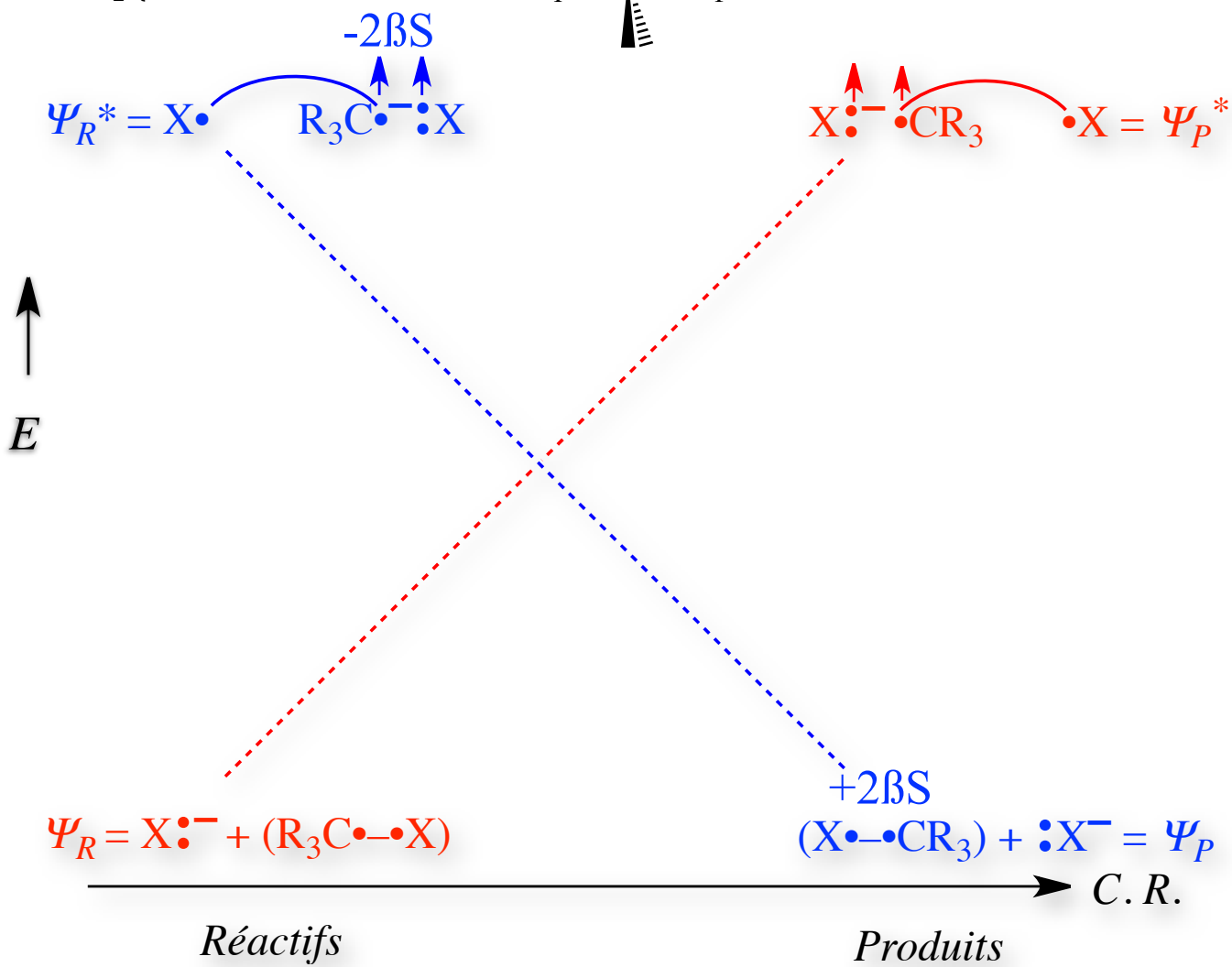

$$\Psi_P \propto \left| (c\overline{x_l} + x_l\overline{c})x_r\overline{x_r} \right|$$

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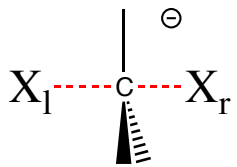

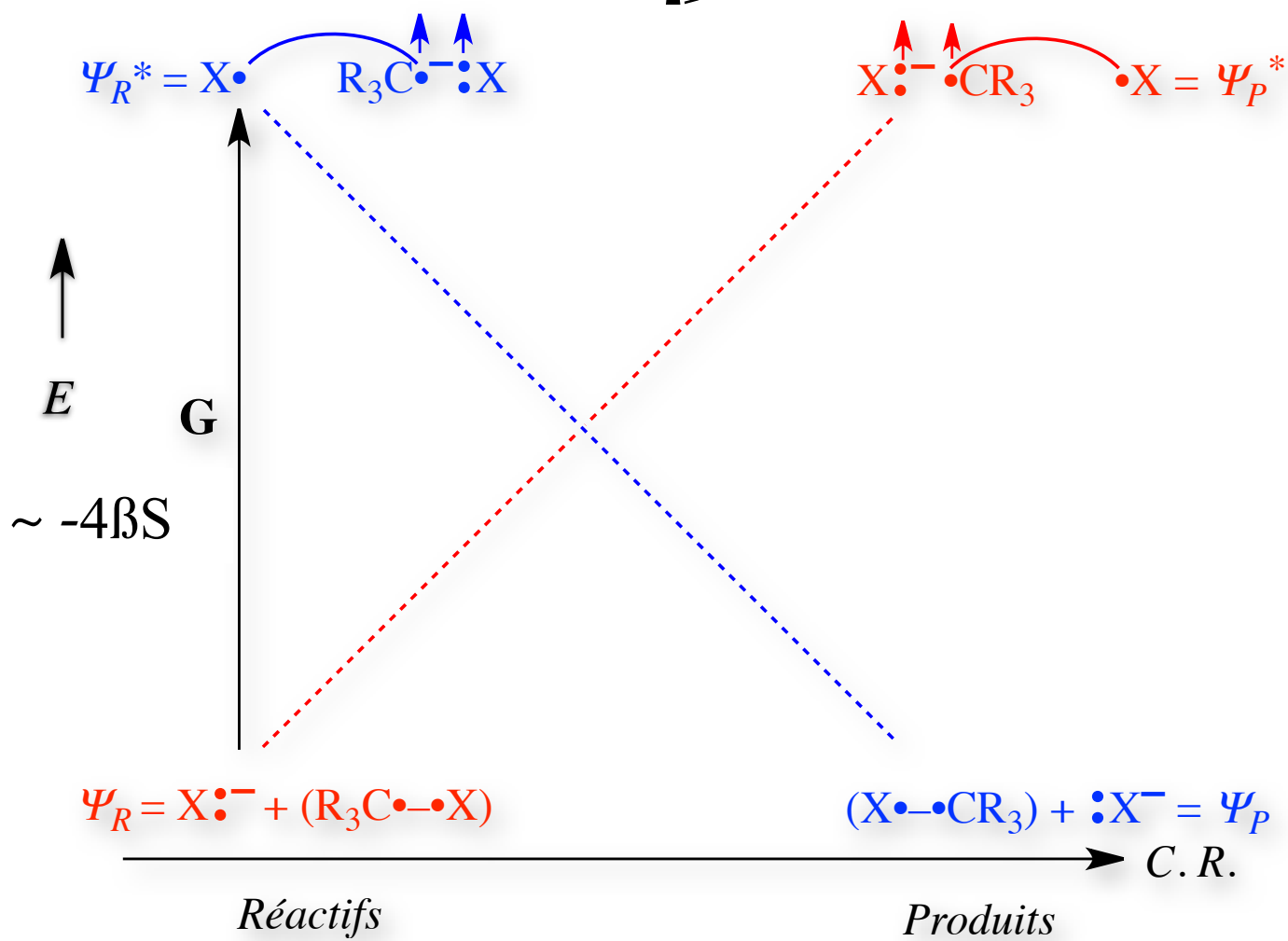

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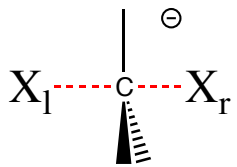

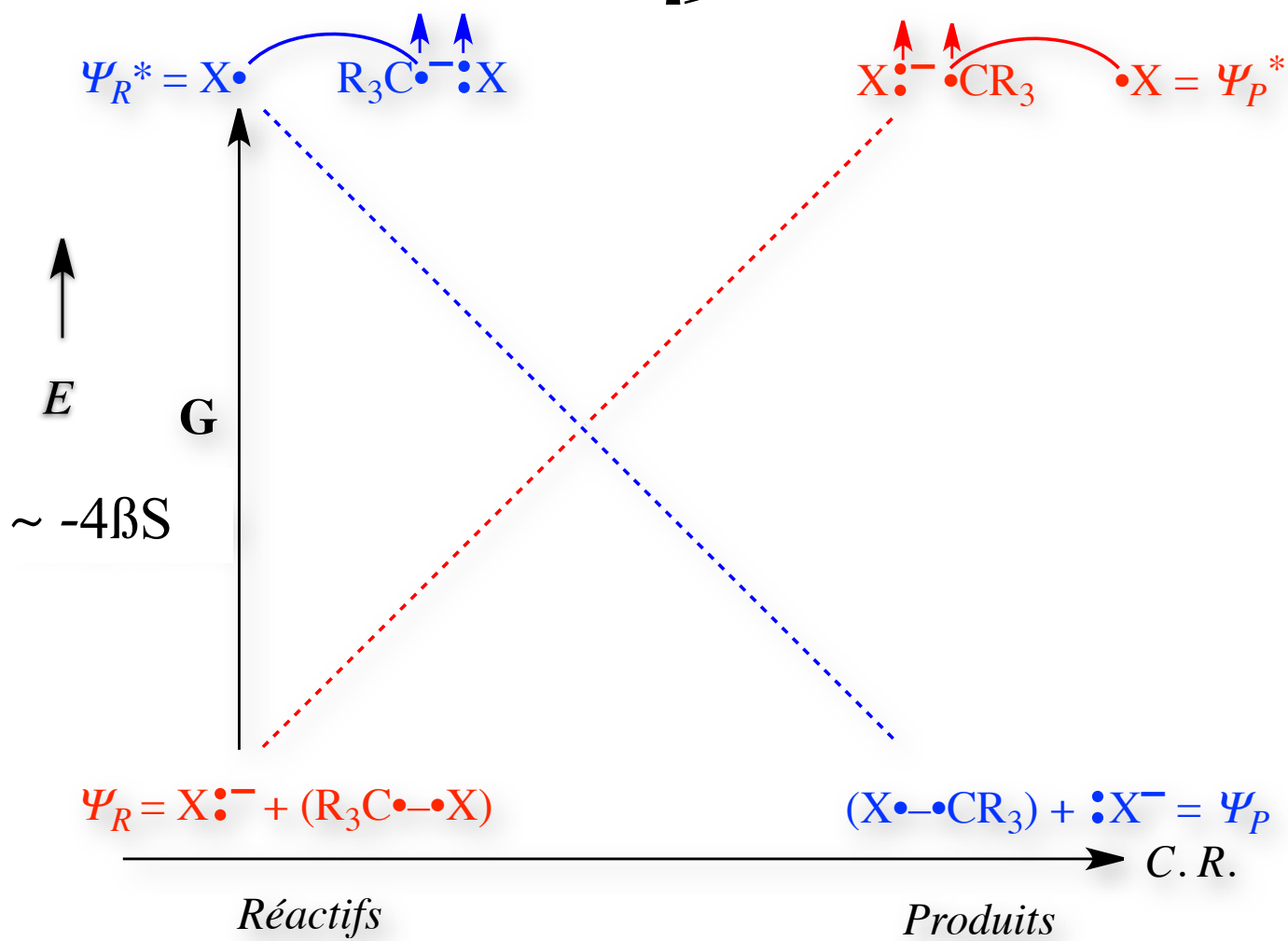

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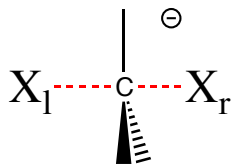

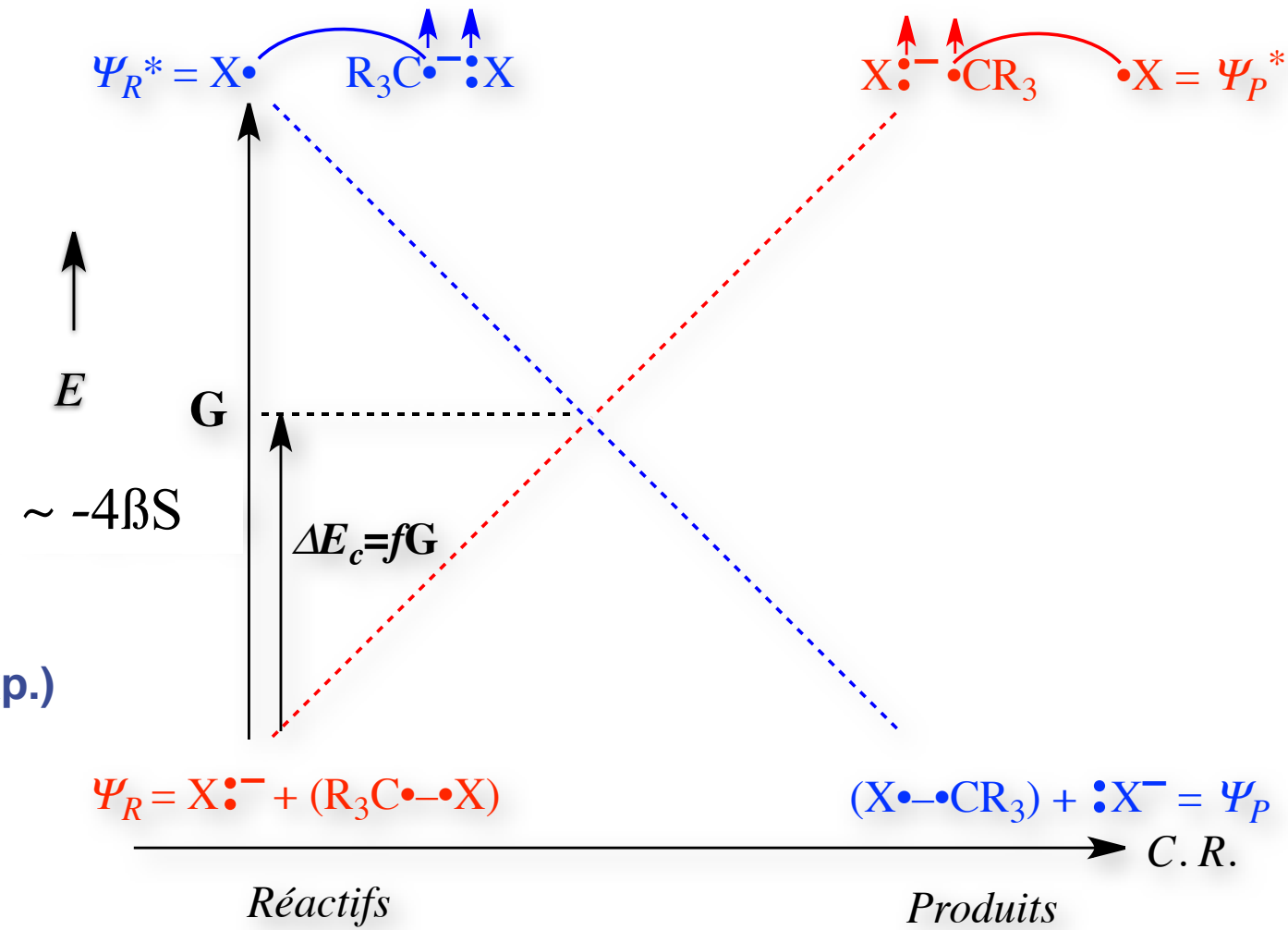

G : reactants' property (exp.)

f : curvature factor

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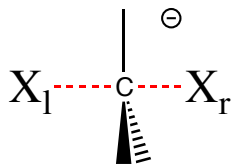
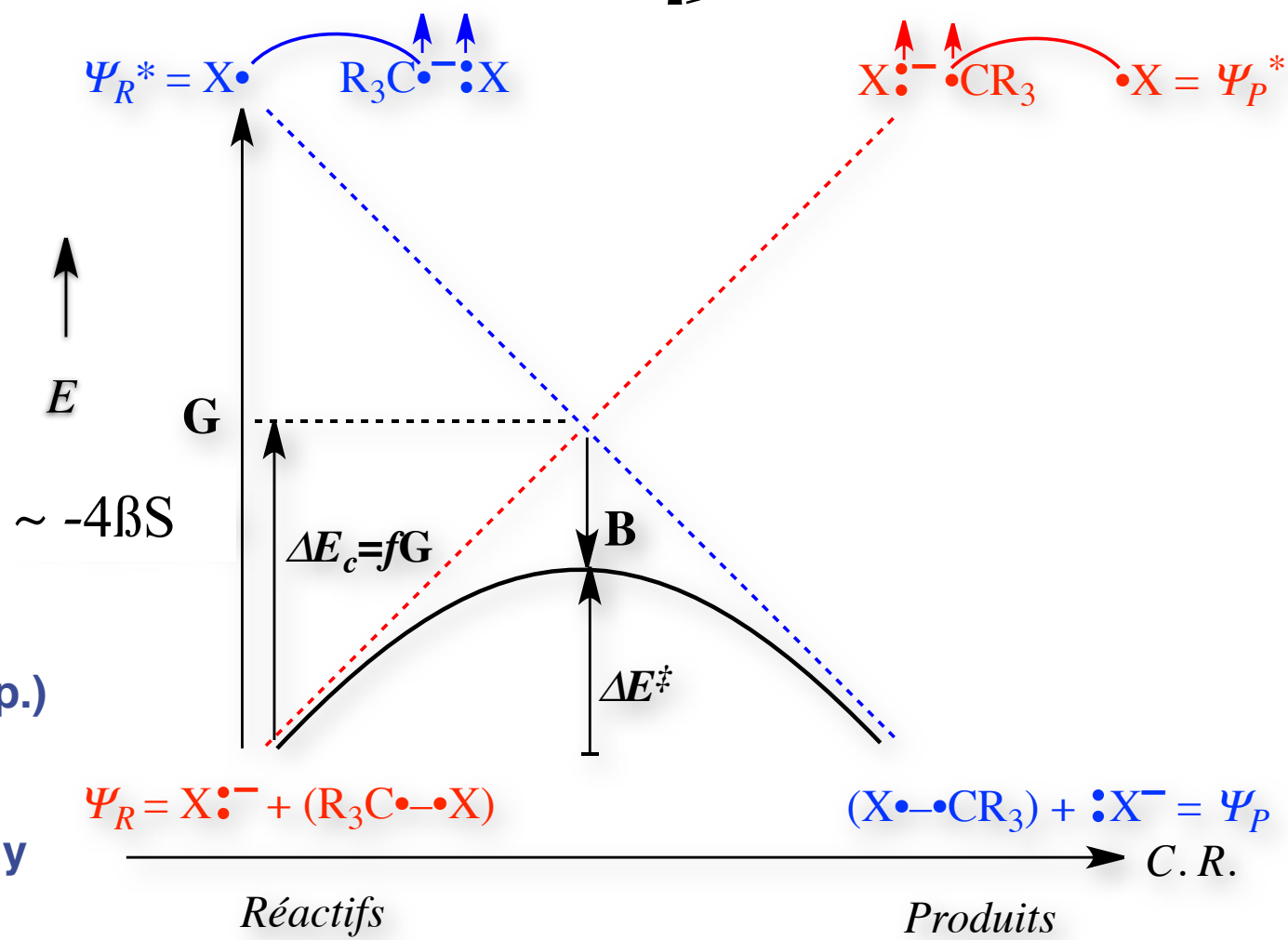


$$\Delta E^{\neq} = f\,G - B$$



G : reactants' property (exp.)

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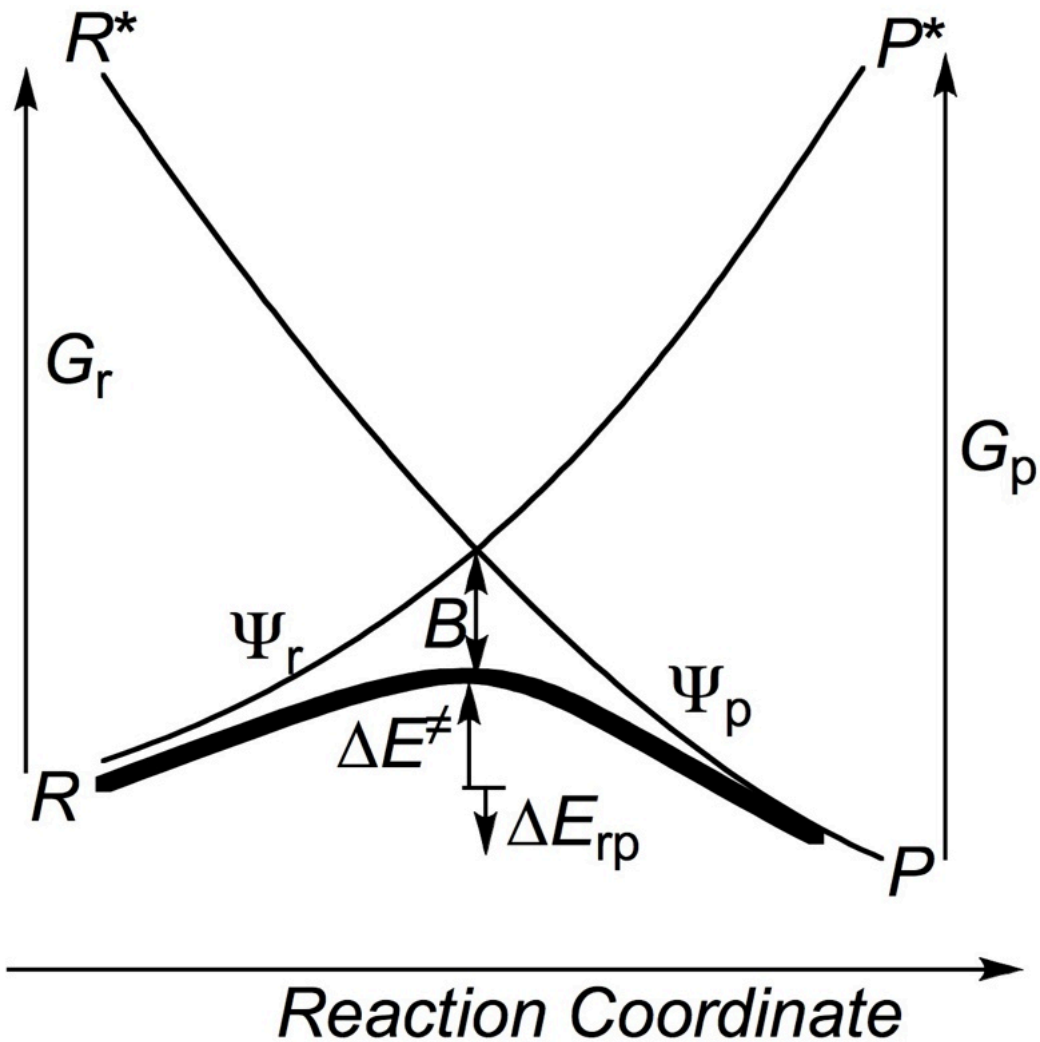
B : resonance energy

Principles

- Extended formula for the two-state diagrams :

$$\Delta E^{\ddagger} \approx f_0 G_0 - B + 0.5\,\Delta E_{RP} + 0.5\,\frac{\Delta E_{RP}^2}{G_0}$$



Principles

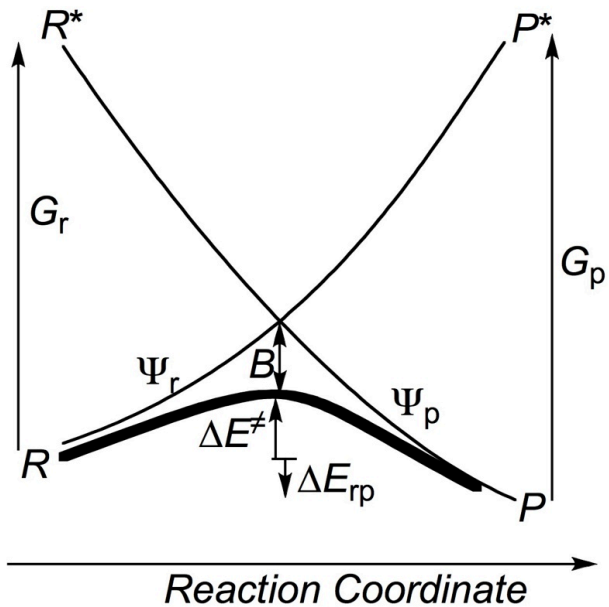
- Basic ingredients of the VB diagrams :

  - **G : promotion energy** : R→R* is an excited diabatic state which prepare the reactants ground state for the bonding changes from R to P.

  - ***f*** **:** measure the **intrinsic «smoothness»** of the electronic structure change in R and P

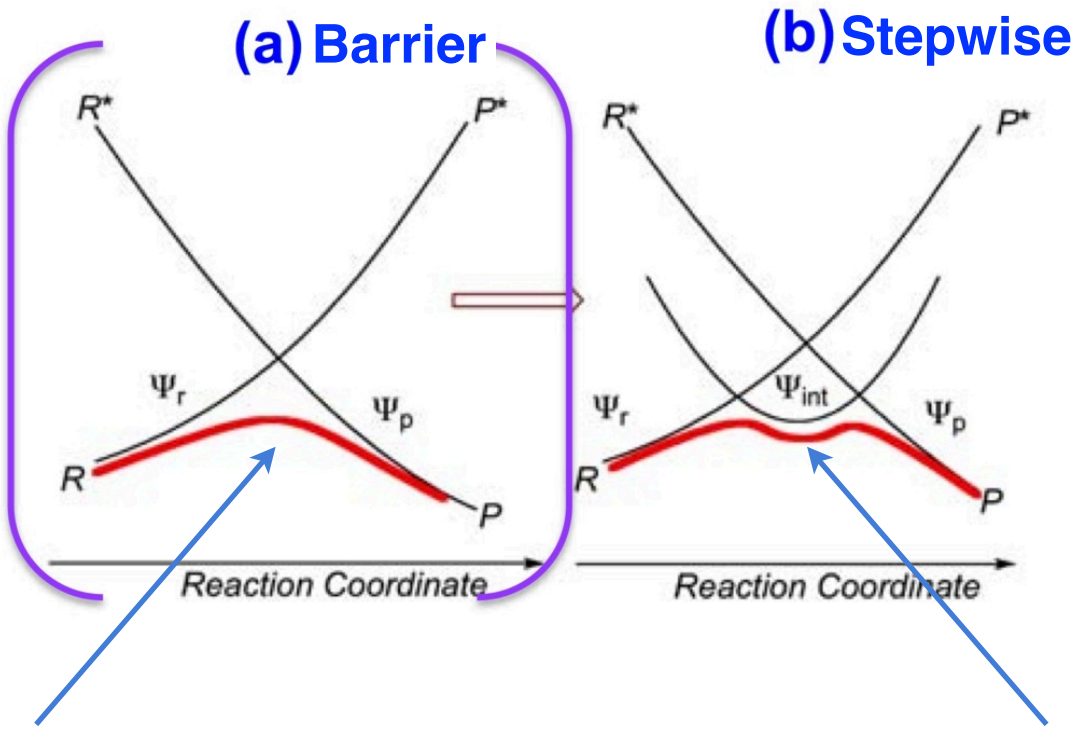
  ⇒ *f*G : gauges the total deformation and repulsive interactions R have to experience to achieve resonance with P

  - **B : resonance energy** of the TS due to VB mixing at the crossing point



Principles

- Two-state (VBSCD) vs. multi-state diagrams (VBCMD) :



R and P mix to form the barrier and the TS for an elementary process

The intermediate has a different electronic structure than R and P («internal catalysis»)

G expressions

- How to derive quantitative expressions for G ?

The promoted states involve two elementary excitations, depending on whether there are **changes in the oxidations states** of fragments or not

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2) count the **number of electrons on each fragment**

3) **does this number change** during reaction ? → **YES** : **change** of ox. state

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NO

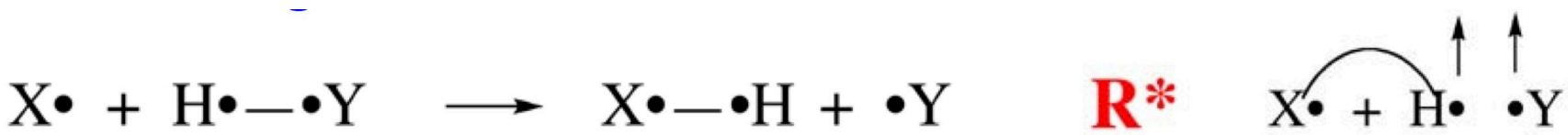
YES

G expressions

- **Rule 1** : no change in oxydation state :
  - What happens during R→R* promotion :

1) Bonds which are broken are decoupled to their triplet state in R*

2) Electrons are paired anew as in P

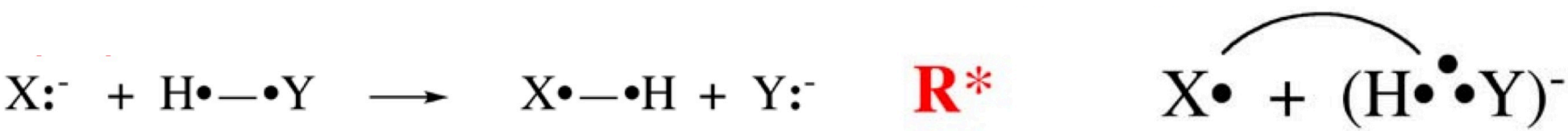


$$\Rightarrow G_r \approx \Delta E(S \rightarrow T)$$

G expressions

- **Rule 2** : change in the oxydation state :
  - What happens during R→R* promotion :

    Charge transfer from the fragment being oxydized (lose 1e⁻) to the fragment being reduced (gain 1e⁻)



$$\Rightarrow G_r \approx IP(X:) - EA(H-Y)$$

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$$\Rightarrow G_r \approx IP(X:) - EA(H - Y)$$

- How to get ΔE(S→T), IP, EA ?
  - Accurate computations (not specially VB !)
  - From experiments

Illustrations

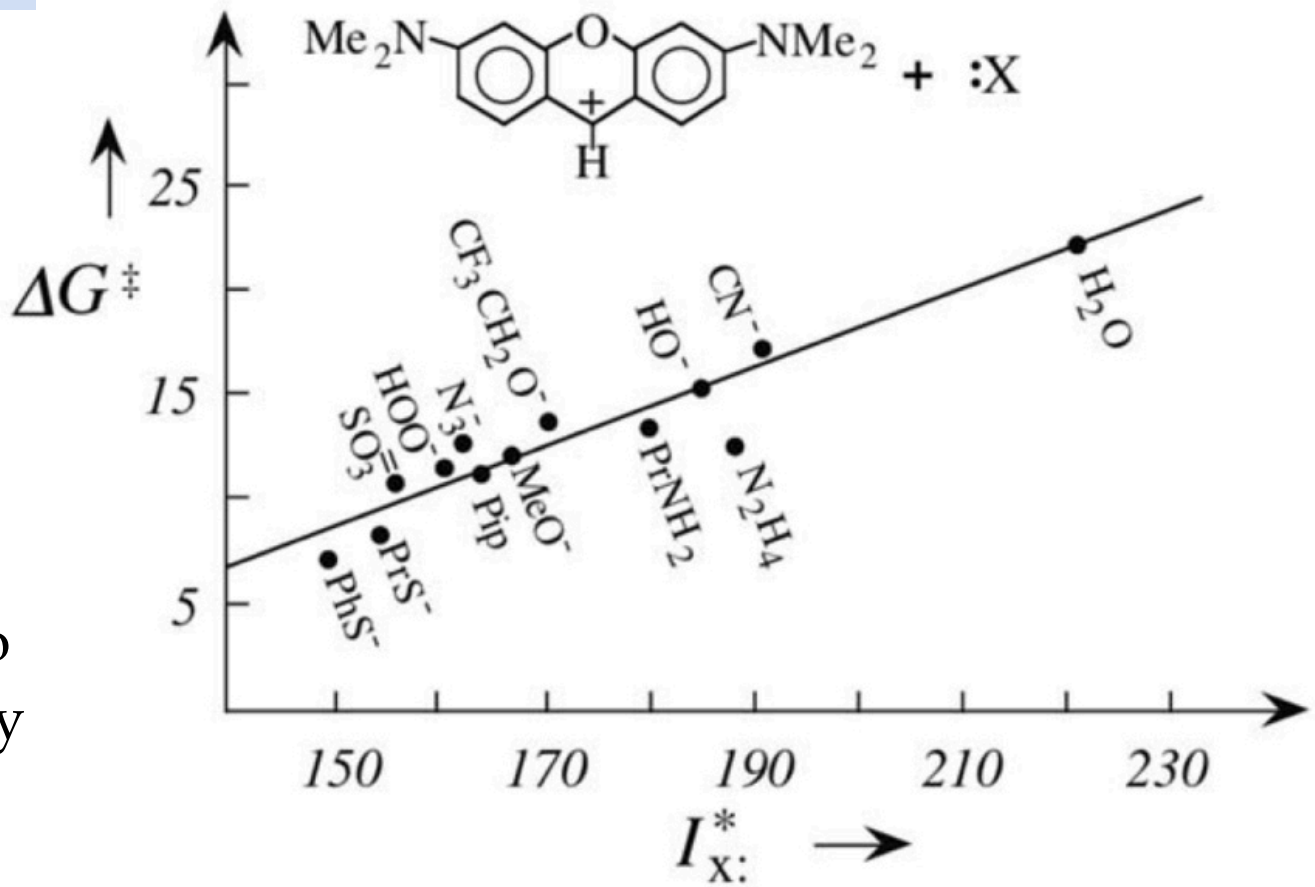
- Anion/Cation recombination : **$X:^- + R^+ \rightarrow X\text{-}R$**

Rule 2 : $G_r \approx IP(X^- :) - EA(R^+)$

In this serie the carbocation

R^+ is common

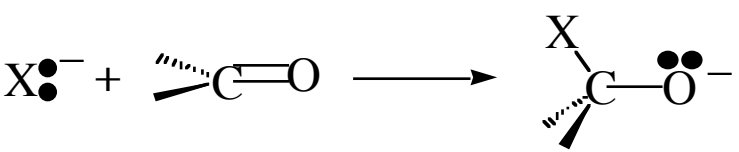
➡ VB diagram bring order to the concept of nucleophilicity

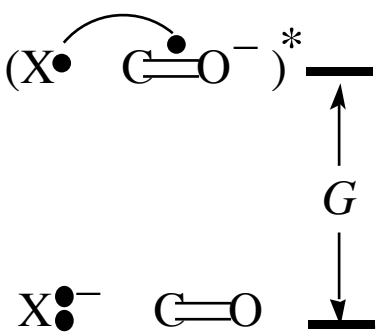


Illustrations

- Nucleophilic addition :

Rule 2 : $G_r \approx IP(X^- :) - EA(R^+)$





$G = I^*_{X:} - A^*_{C=O}$

Illustrations

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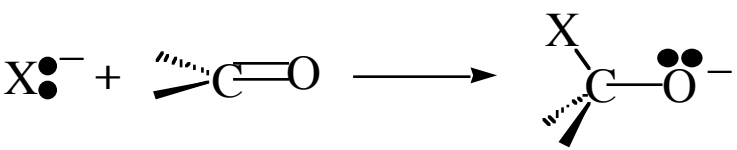

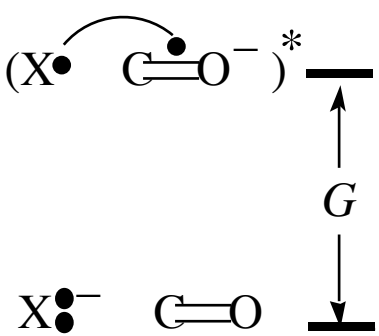

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First set : localized

$X:^-$ = F^-, CN^-, HO^-, HOO^-

$CF_3CH_2O^-$, CH_3O^-,

$\Delta E^{\neq} = f_1(IP(X^-)) + cte$

Second set : delocalized

PhS^-, PhO^-, N_3^-, NO_2^-, AcO^-

$\Delta E^{\neq} = f_2(IP(X^-)) + cte$

$f_2 > f_1$

Illustrations

- Nucleophilic addition :

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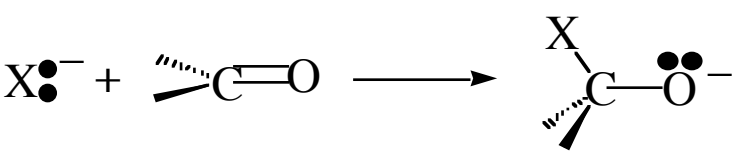
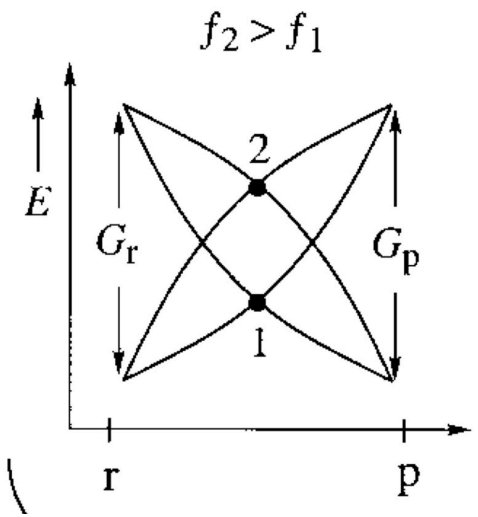
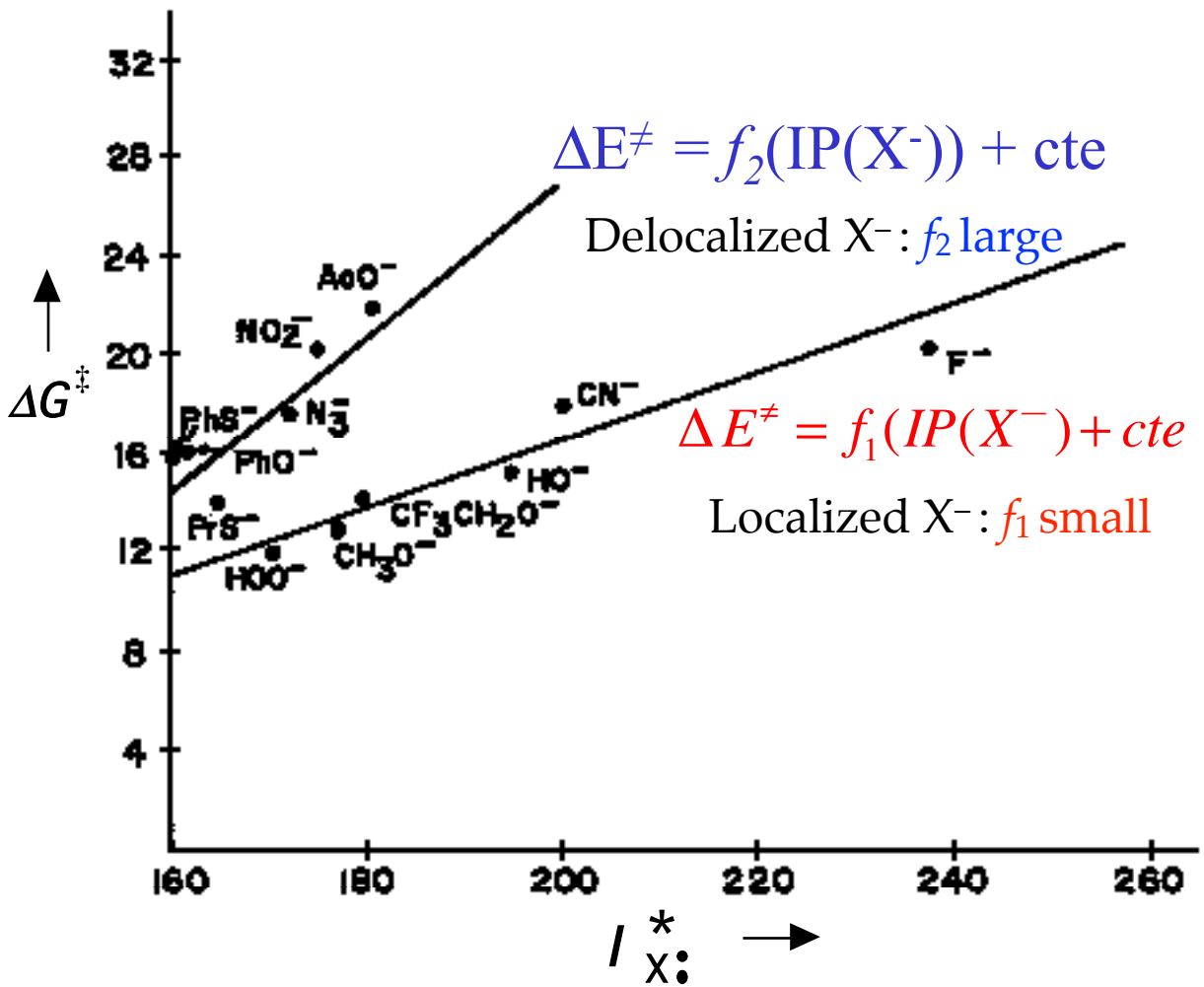






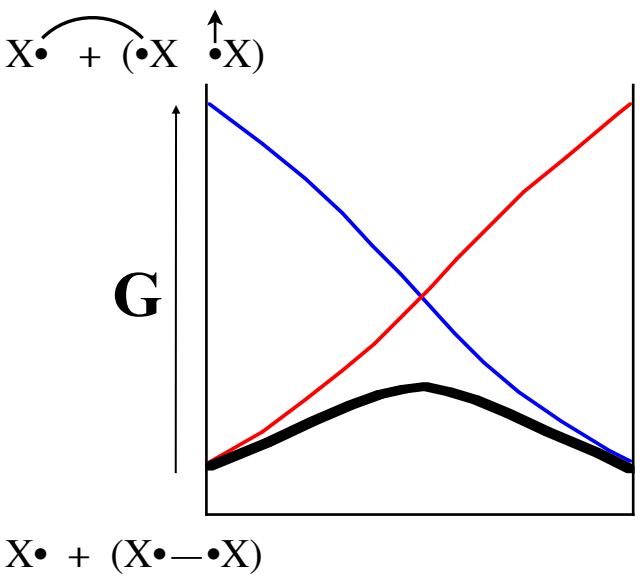
Illustrations

- Radical exchange reactions

Stability or unstability of X_3• clusters (X= H, F, Cl, Br, I, Li, Na, etc.)

X• + X-X → [X--X--X]• → X–X + X•

$$\text{Rule 1}: \Rightarrow G \approx \Delta E_{ST}(X-X) \propto 2D_e$$



Strong bonds (H_3):
Large barrier

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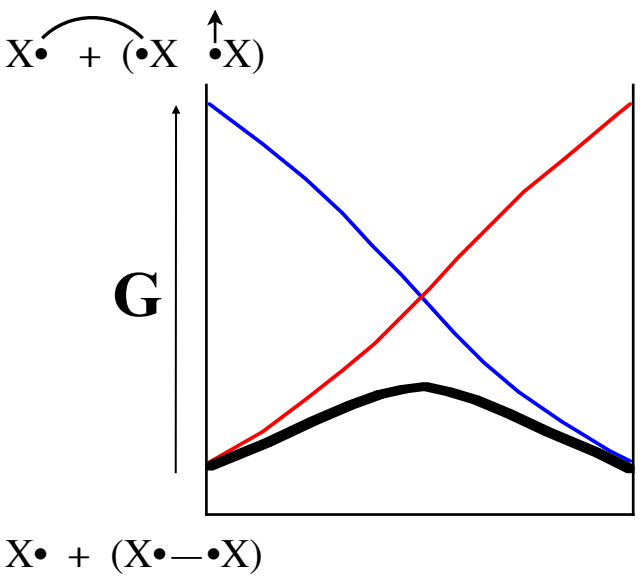

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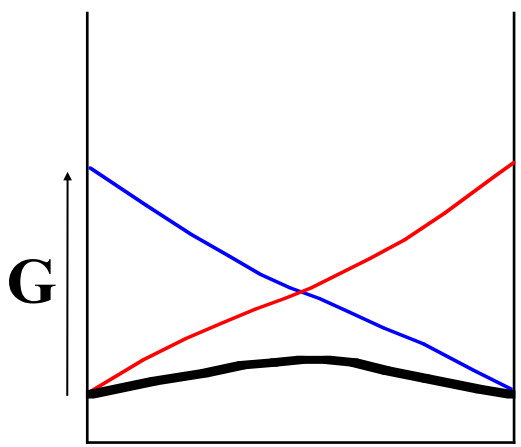

Weaker bonds (Cl_3):
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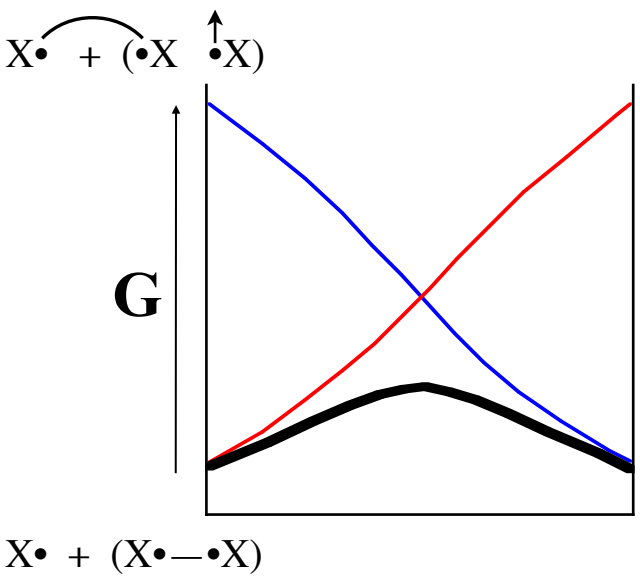

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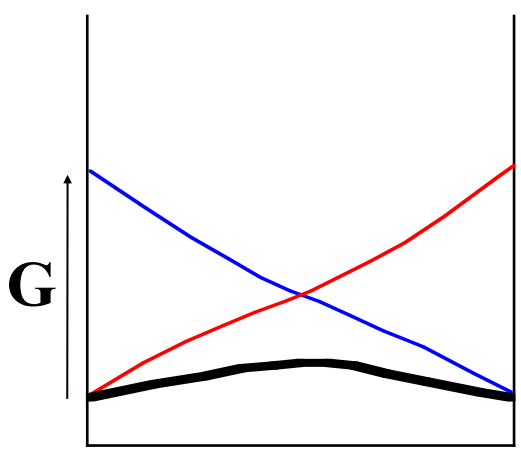

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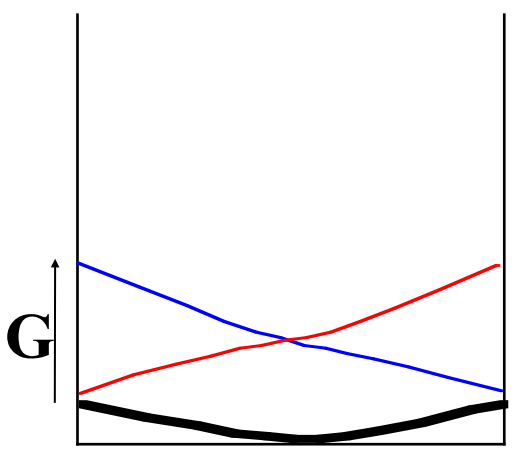
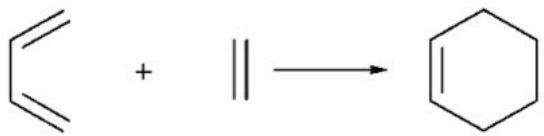


Weak bonds (Li_3):
Stable cluster

Illustrations

- Allowed / forbidden cycloadditions

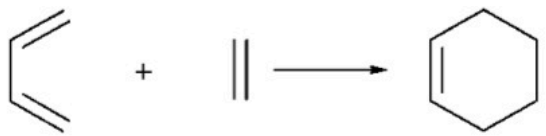


(D) (O) [4+2]

[2+2]

Illustrations

- Allowed / forbidden cycloadditions



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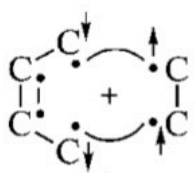
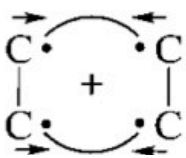
R* 

R* 

Rule 1 : $G = \Delta E_{ST}(D) + \Delta E_{ST}(O)$

$G = 2\Delta E_{ST}(O)$

with : $\Delta E_{ST}(O) > \Delta E_{ST}(D)$

➡ G lower for [4+2] cycloaddition

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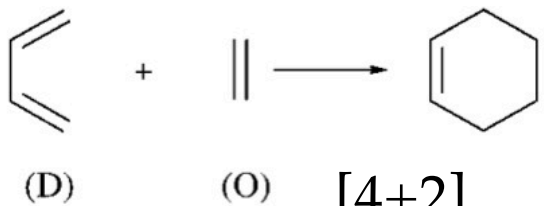

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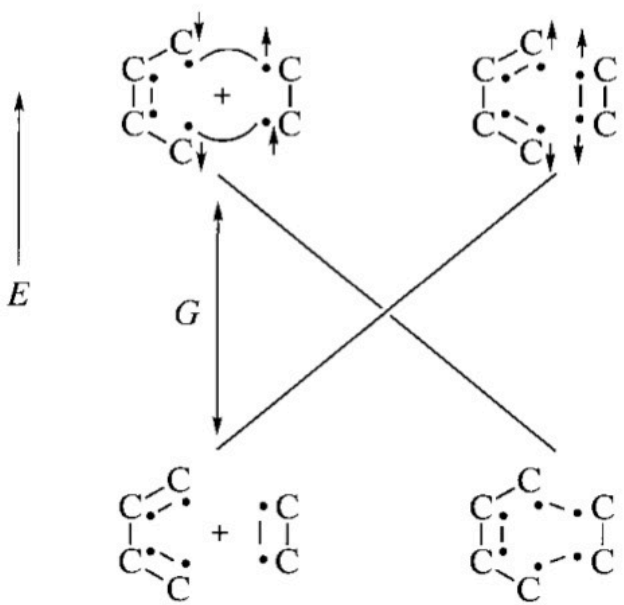
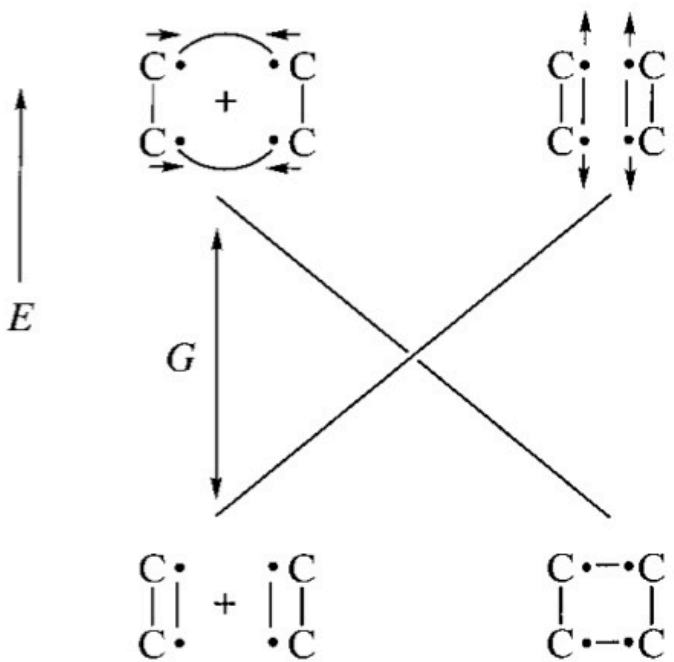
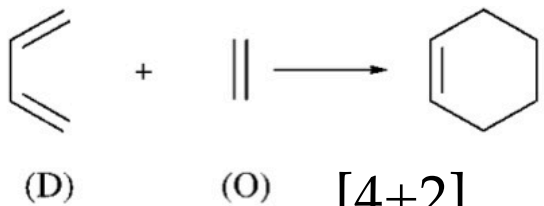
[2+2]





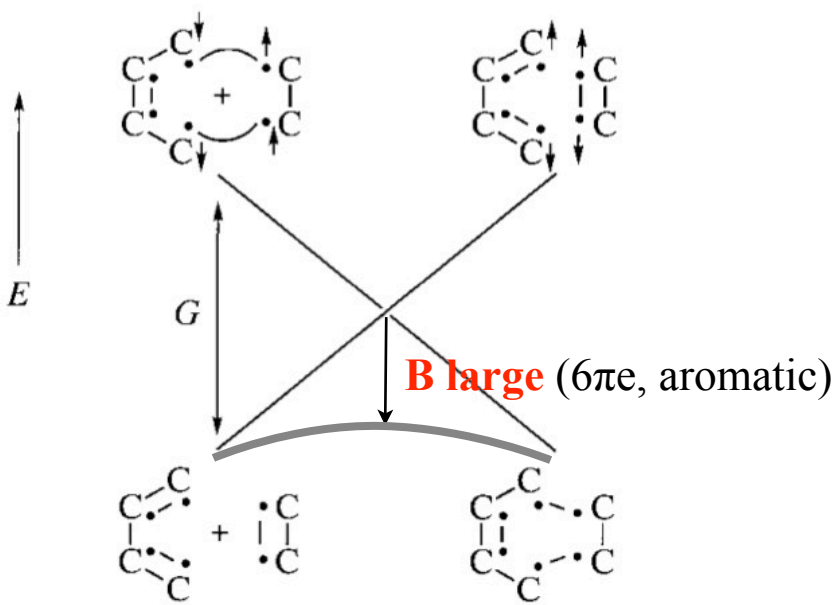
Illustrations

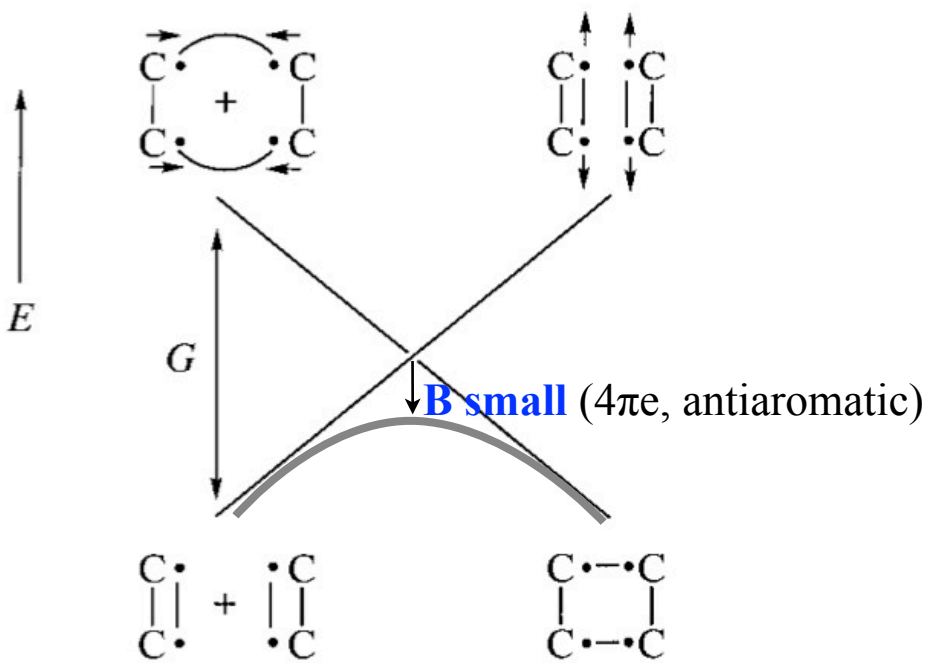
- Allowed / forbidden cycloadditions



[4+2]

[2+2]





➡ G lower and B larger for [4+2] cycloaddition

$$\Delta E = fG - B$$

Illustrations

- Allowed / forbidden cycloadditions

Formally Allowed

[2+2+2] [4+2]

Higher thermodynamic driving but much higher barrier...

$\Delta H = -67$ kcal/mol

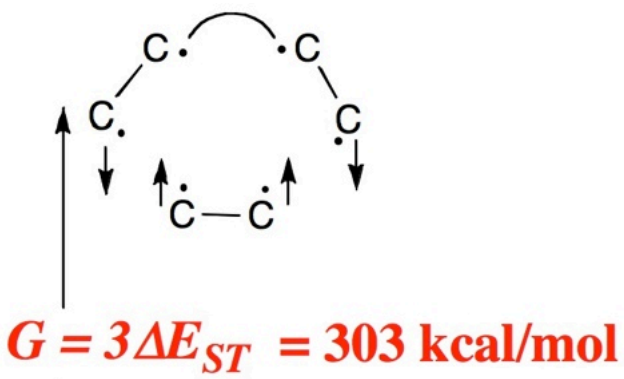
$\Delta H^{\neq} = 49$ kcal/mol

$\Delta H = -44$ kcal/mol

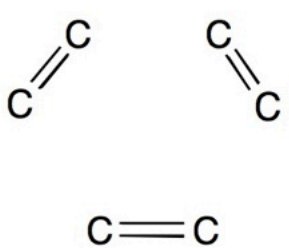
$\Delta H^{\neq} = 22$ kcal/mol

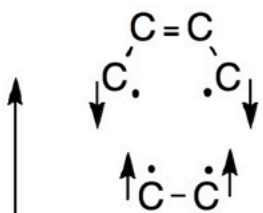
Illustrations

- Allowed / forbidden cycloadditions

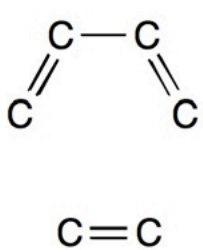


$G = 3\Delta E_{ST} = 303$ kcal/mol





$G = \Delta E_{ST}^{(diene)} + \Delta E_{ST}^{(ethene)} = 179$ kcal/mol

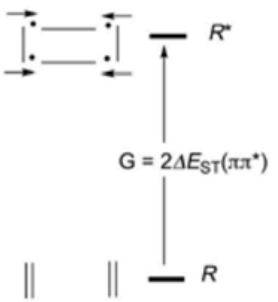


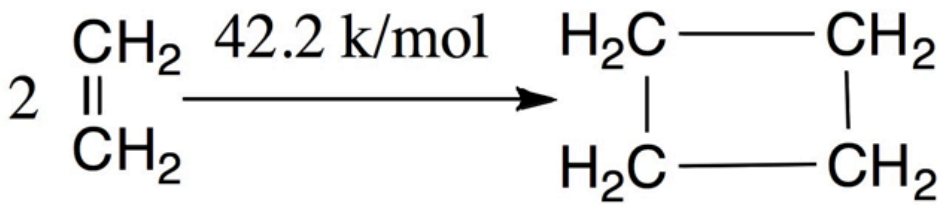
➡ G much higher for [2+2+2] cycloaddition

Illustrations

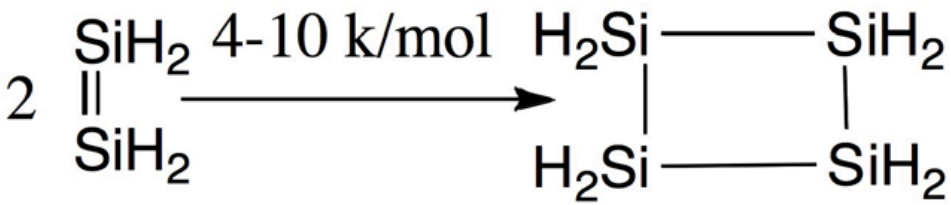
- Allowed / forbidden cycloadditions
  - G involve S→T decoupling of the two π bonds :

    Formally Forbiden





$G_C = 2\Delta E_{ST}(\pi\pi^*) = 202$ kcal/mol



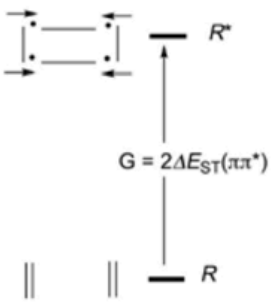
$G_{Si} = 2\Delta E_{ST}(\pi\pi^*) = 80$ kcal/mol

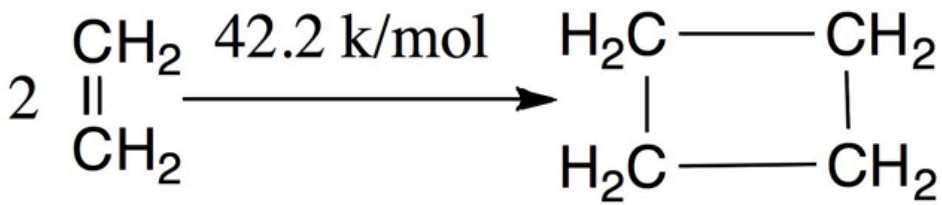
- Estimation using the formula ($\Delta E^{\neq} = fG - B$) and $f = 0.3$ (typical value) lead to a barrier difference of 40 kcal.mol^{-1} for Si vs C : not bad !

Illustrations

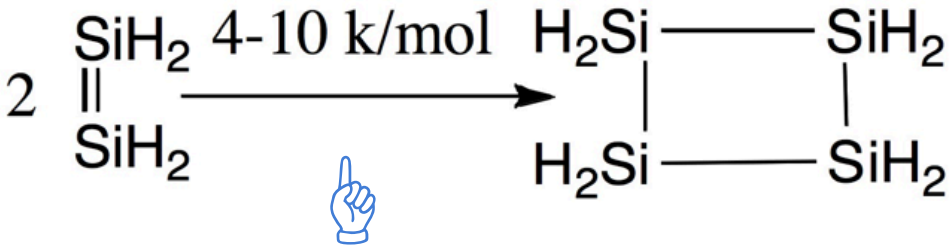
- Allowed / forbidden cycloadditions
  - G involve S→T decoupling of the two π bonds :

    Formally Forbiden





$G_C = 2\Delta E_{ST}(\pi\pi^*) = 202$ kcal/mol

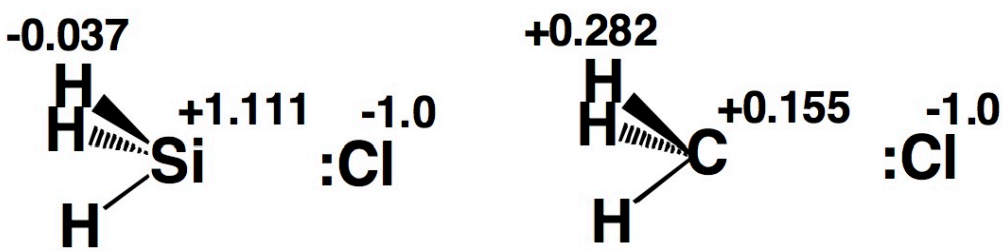


$G_{Si} = 2\Delta E_{ST}(\pi\pi^*) = 80$ kcal/mol

It is even faster than the (formally allowed) Diel-Alder reaction with G=179 kcal.mol^{-1} !

Illustrations

- SN2(C) vs. SN2(Si) - Origin of hypercoordination :

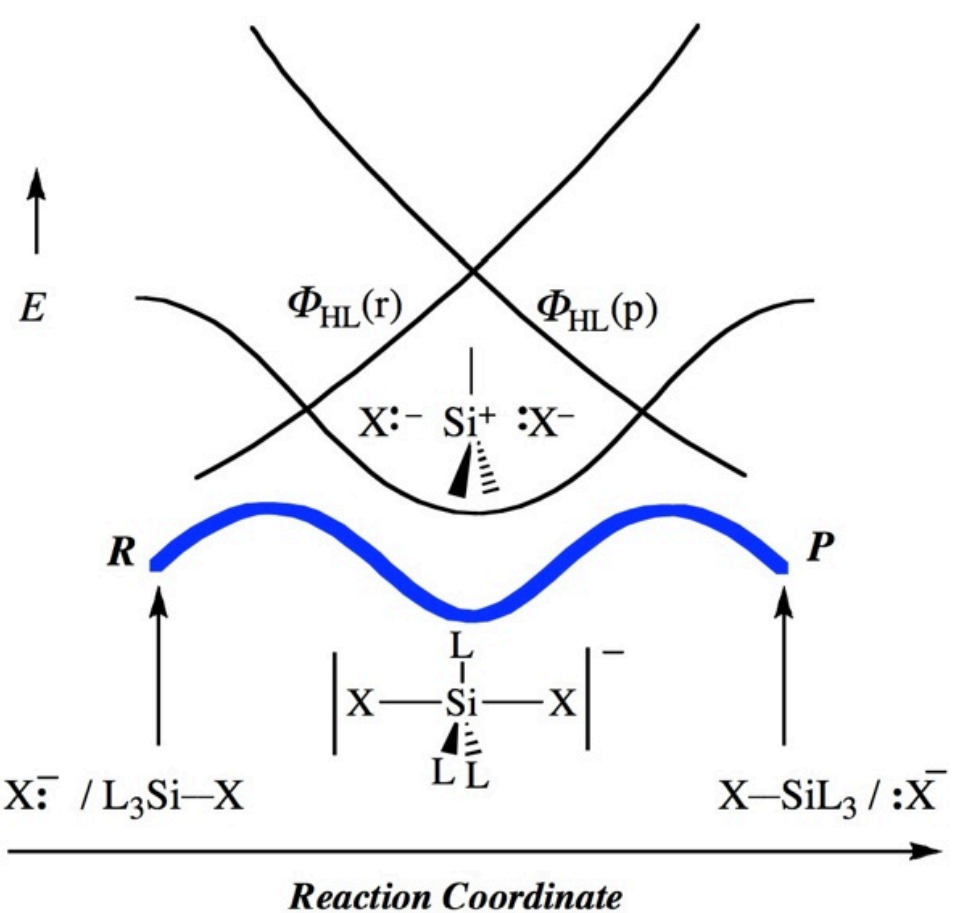


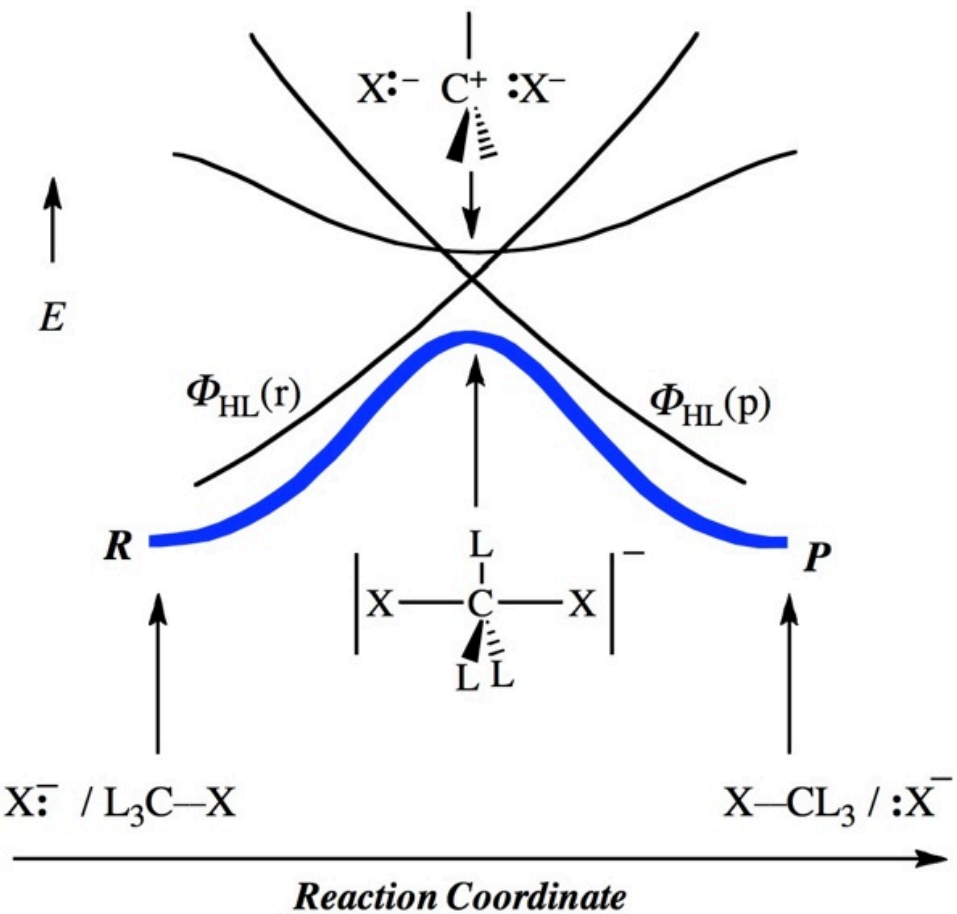
Positive charge localization on Si vs. delocalization on C

⇒ Si small ion allowing close approach of anions and a significant electrostatic stabilization of its ionic structure

Illustrations

- SN2(C) vs. SN2(Si) - Origin of hypercoordination :





Illustrations

- Barrier in radical exchange reactions :

$$X^{\bullet} + H\text{–}X \rightarrow [X\ldots H\ldots X]^{\bullet} \rightarrow X\text{–}H + X^{\bullet}$$

	$\Delta E^{\neq}$ (kcal/mol)
FHF	20.9
ClHCl	11.0
BrHBr	8.0

Illustrations

- Barrier in radical exchange reactions :

$$H^{\bullet} + X\text{–}H \rightarrow [H\ldots X\ldots H]^{\bullet} \rightarrow H\text{–}X + H^{\bullet}$$

	$\Delta E^{\neq}$ (kcal/mol)
HFH	42.5
HClH	18.5
HBrH	12.9

Illustrations

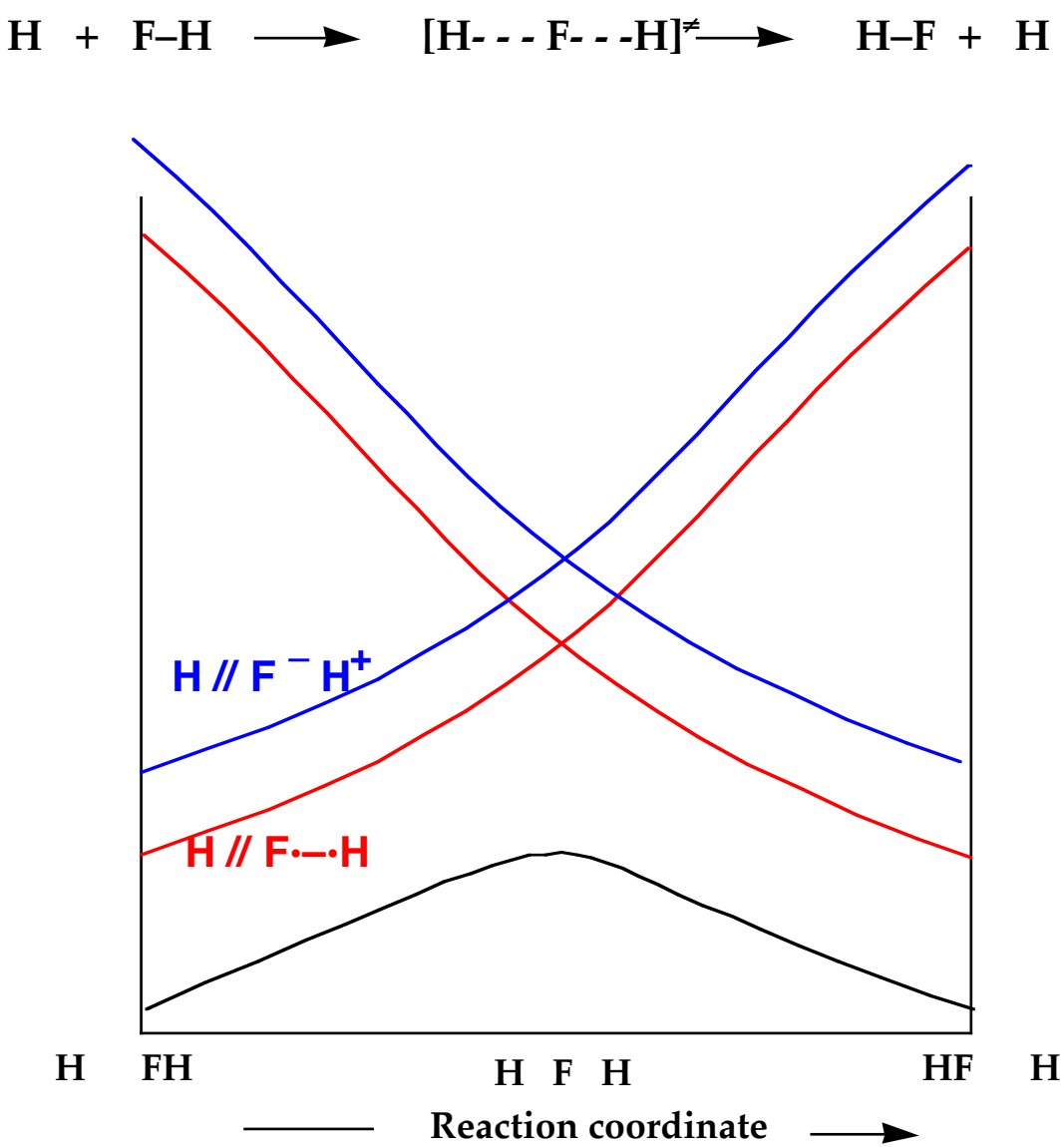
- Barrier in radical exchange reactions :

$$H^{\bullet} + X\text{–}H \rightarrow [H\ldots X\ldots H]^{\bullet} \rightarrow H\text{–}X + H^{\bullet}$$

$$X^{\bullet} + H\text{–}X \rightarrow [X\ldots H\ldots X]^{\bullet} \rightarrow X\text{–}H + X^{\bullet}$$

	$\Delta E^{\neq}$ (kcal/mol)
HFH	42.5
FHF	20.9
HClH	18.5
ClHCl	11.0
HBrH	12.9
BrHBr	8.0

Illustrations

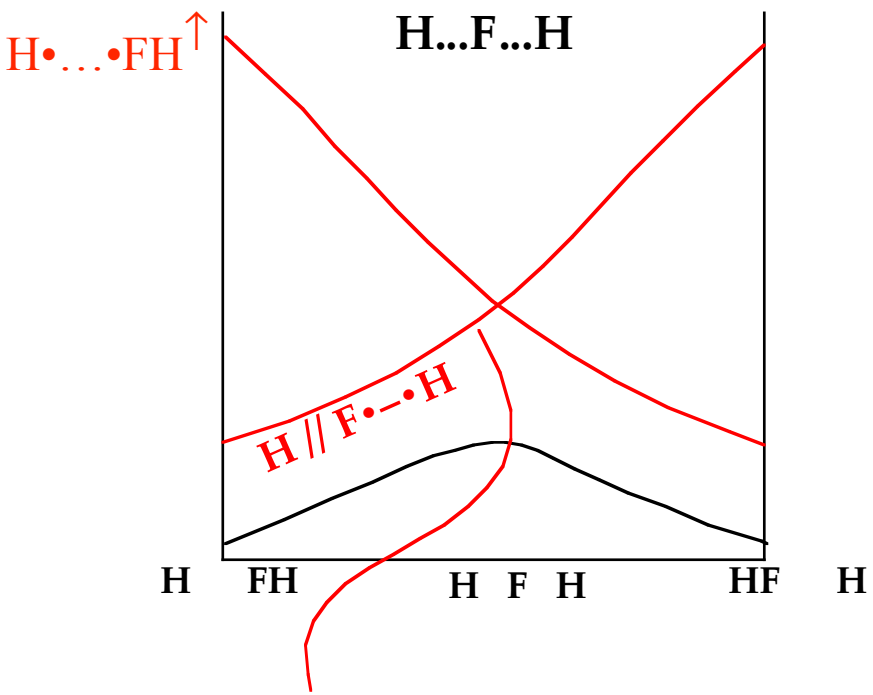


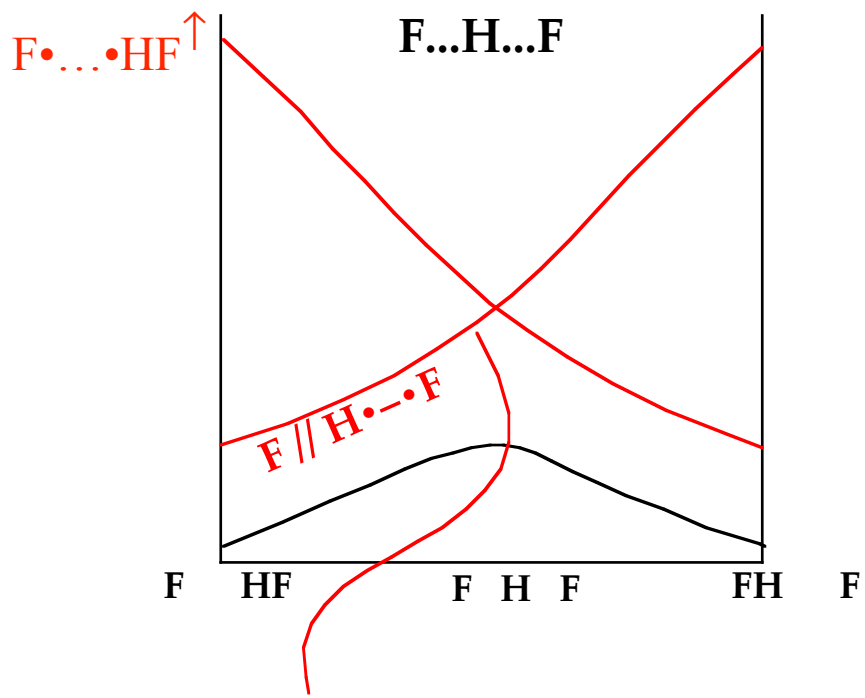
VB state-crossing diagrams

Similar diagrams for FHF reaction...

Illustrations

The covalent curves

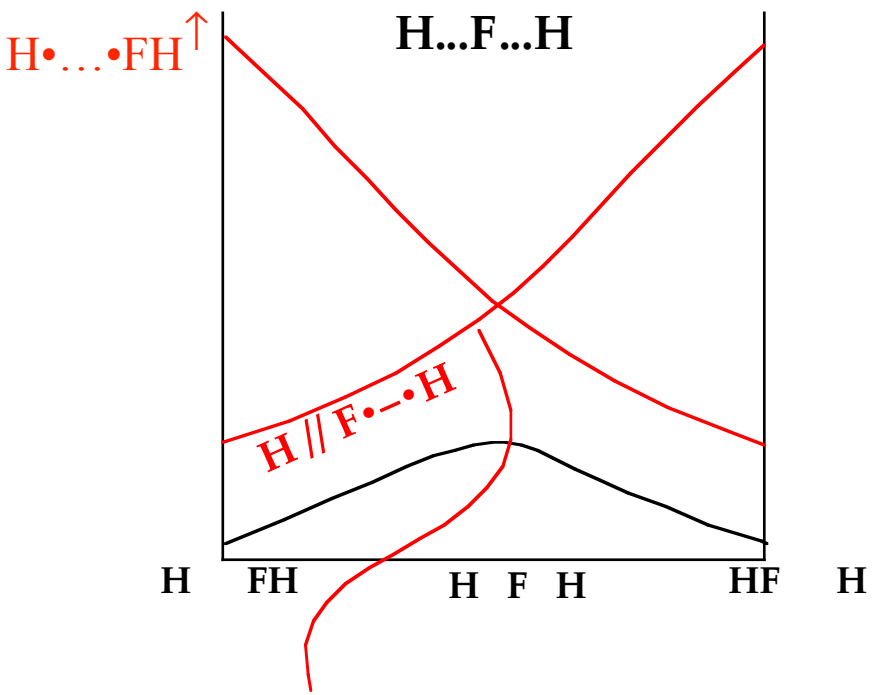




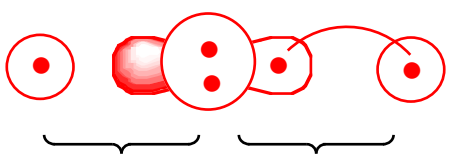
On the basis of covalent structures alone, both reactions should have the same barriers !

Illustrations

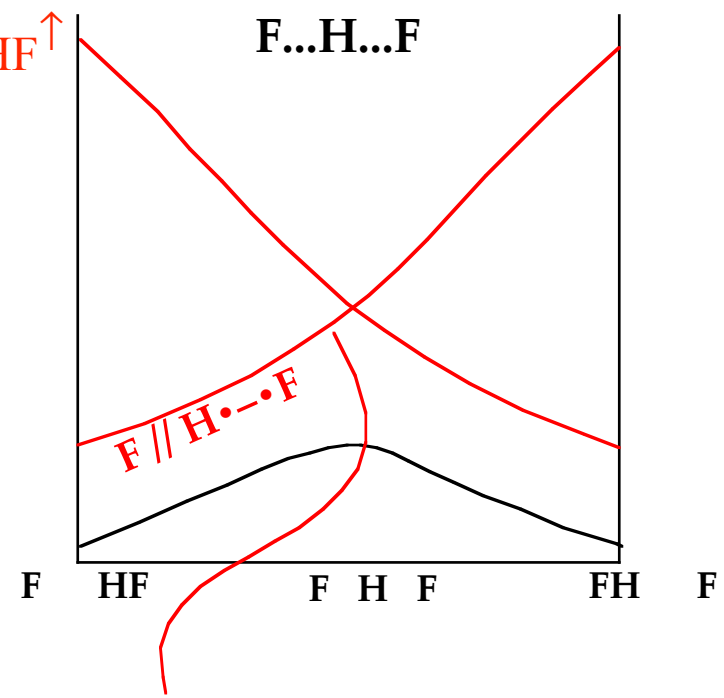
The covalent curves



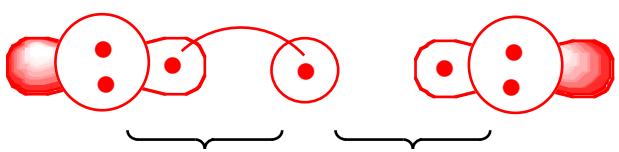
H…F•–•H + mirror image



$\Delta E^{\neq} = 62.6$ kcal/mol



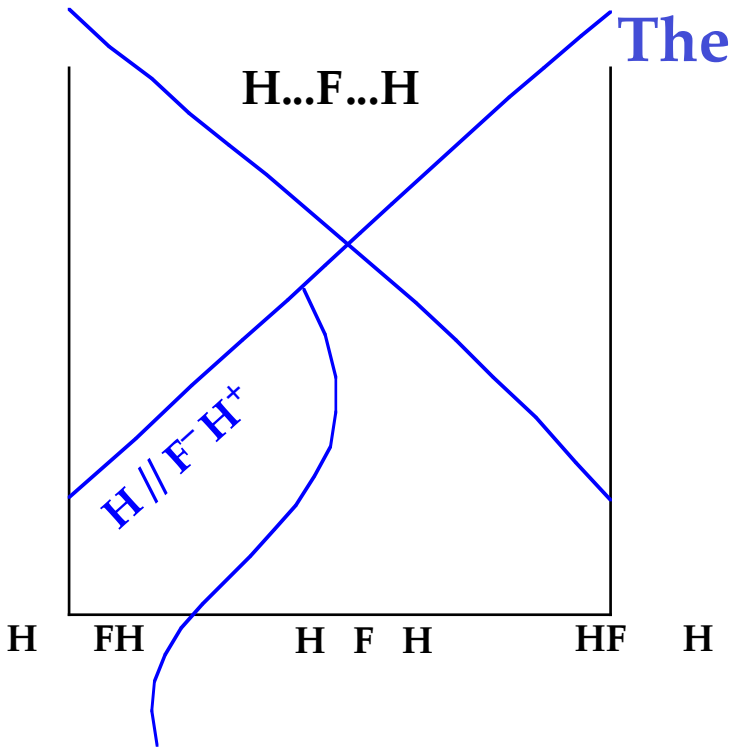
F…H•–•F + mirror image



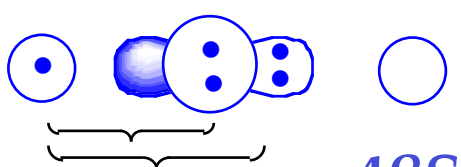
$\Delta E^{\neq} = 60.7$ kcal/mol

Illustrations

The ionic curves



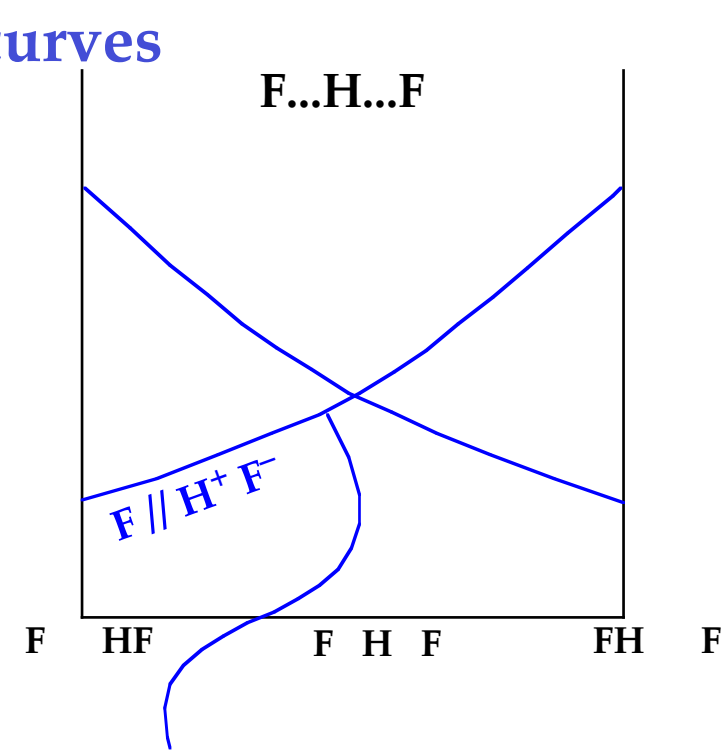
$H^{\uparrow}$.. F^{-}..H^{+} + mirror image



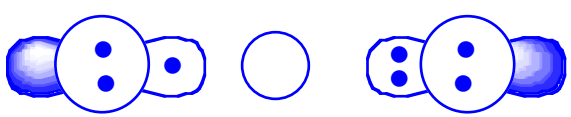
3-e repulsion × 2

$-4\beta S$

The ionic structure is strongly destabilized in the transition state



$F^{\uparrow}$.. H^{+}..F^{-} + mirror image



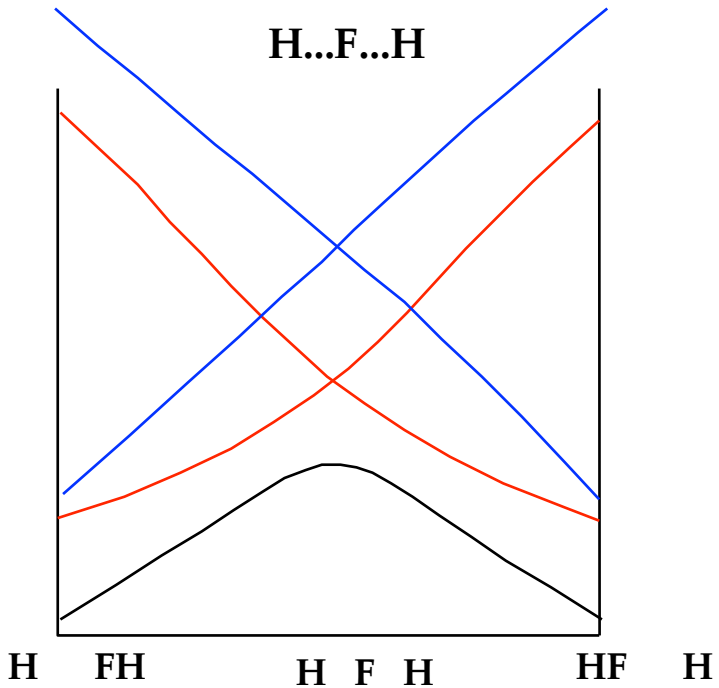
no repulsion

0

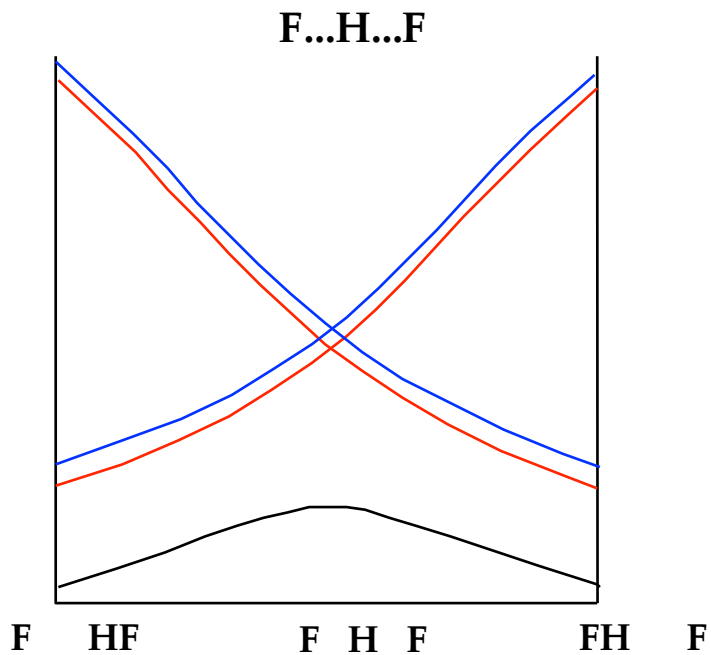
The ionic structure is not destabilized

Illustrations

Covalent + ionic curves



Loss of covalent-ionic RE at the transition state **=> high barrier**

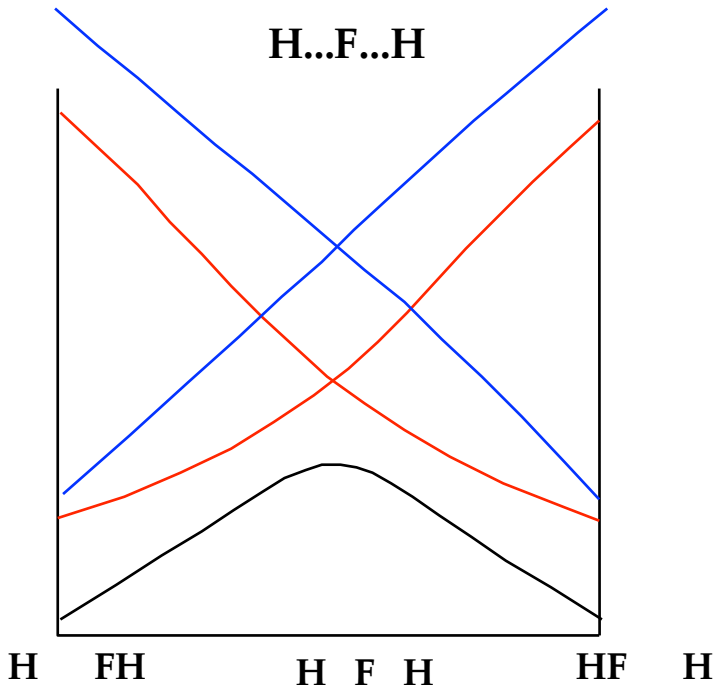


Constant covalent-ionic RE:
=> lower barrier

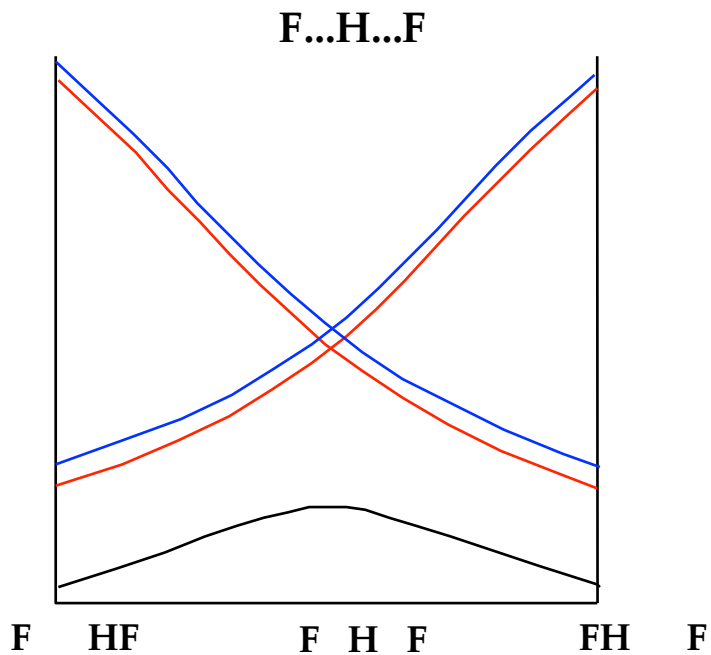
The only factor that differentiate barriers at the TS is the covalent-ionic RE

Illustrations

Covalent + ionic curves



Loss of covalent-ionic RE at the transition state **=> high barrier**

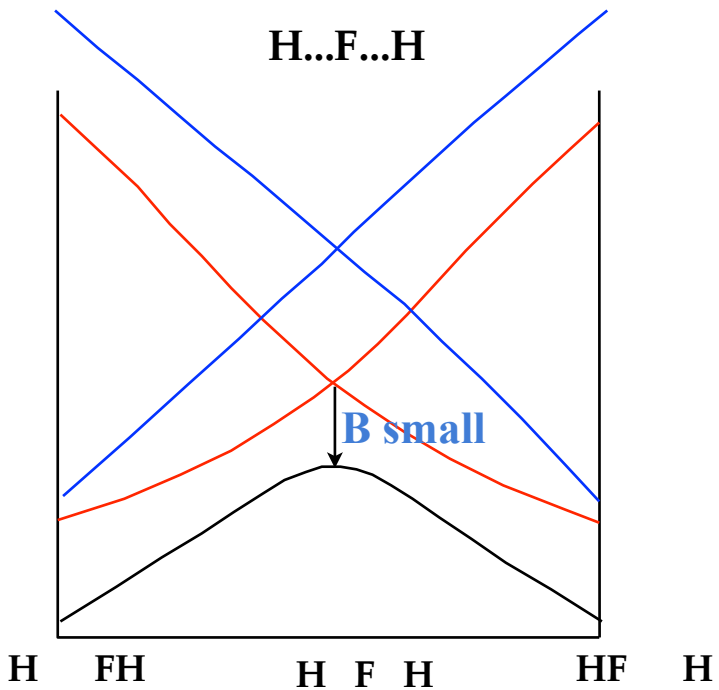


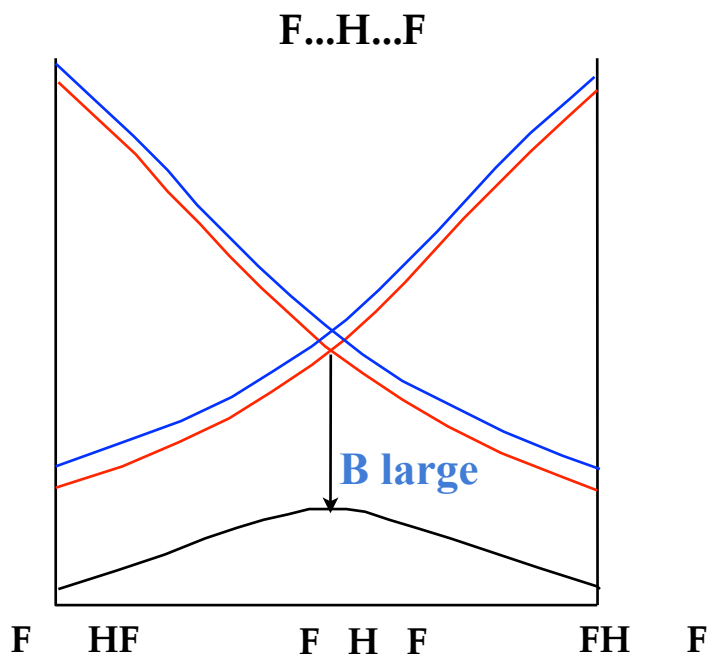
Constant covalent-ionic RE:
=> lower barrier

...and we know (from tutorial 1) that the covalent-ionic RE is very large in H—F

Illustrations

Covalent + ionic curves





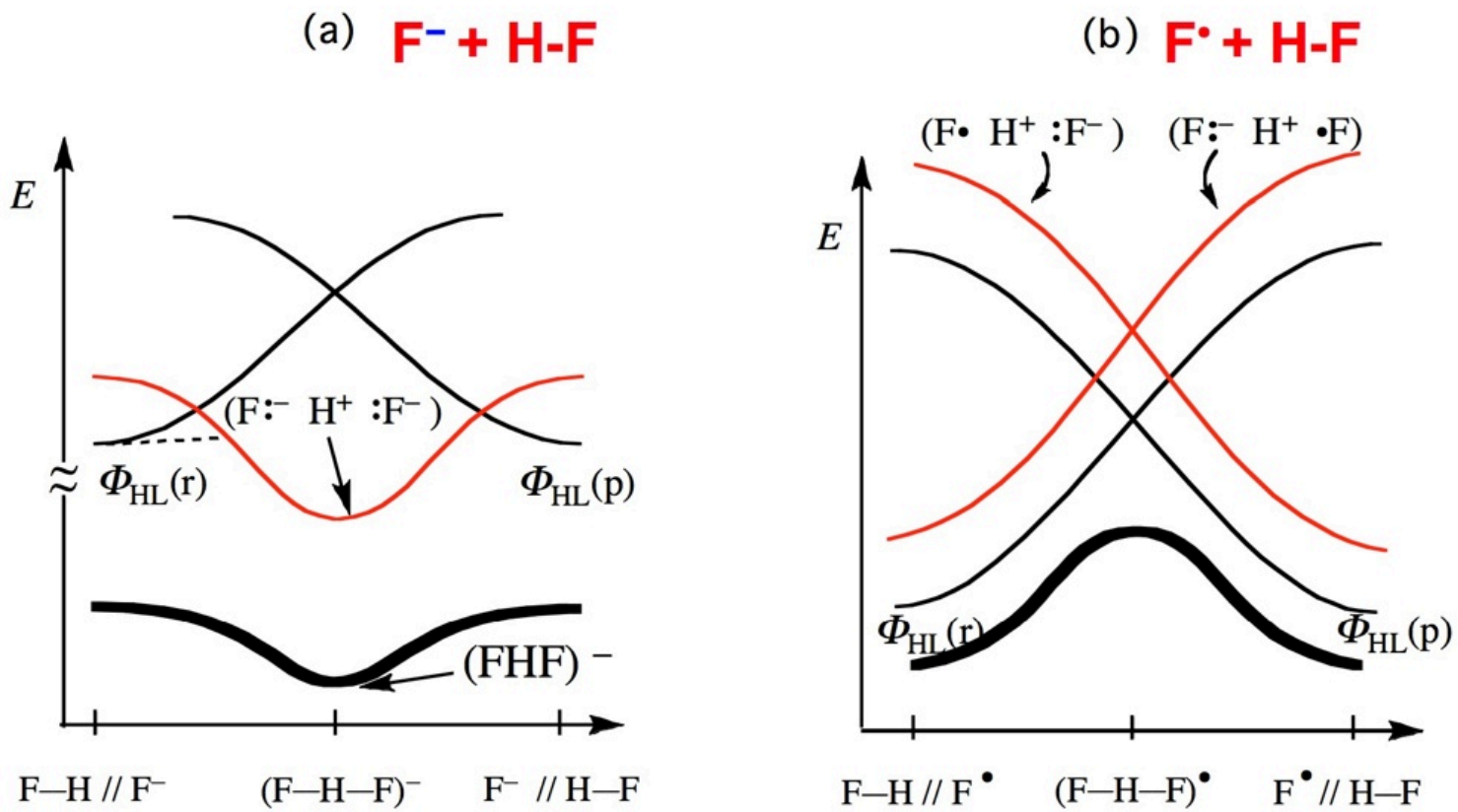
H…F…H vs. F…H…F

Resonance Energies (BOVB): $RE(HFH) < RE(FHF)$ Difference = **22.3** kcal/mol

Reaction barriers (CCSD(T)): $\Delta E^{\neq}(HFH) < \Delta E^{\neq}(FHF)$ Difference = **21.6** kcal/mol

Illustrations

- Multistate diagrams (VBCMD) :

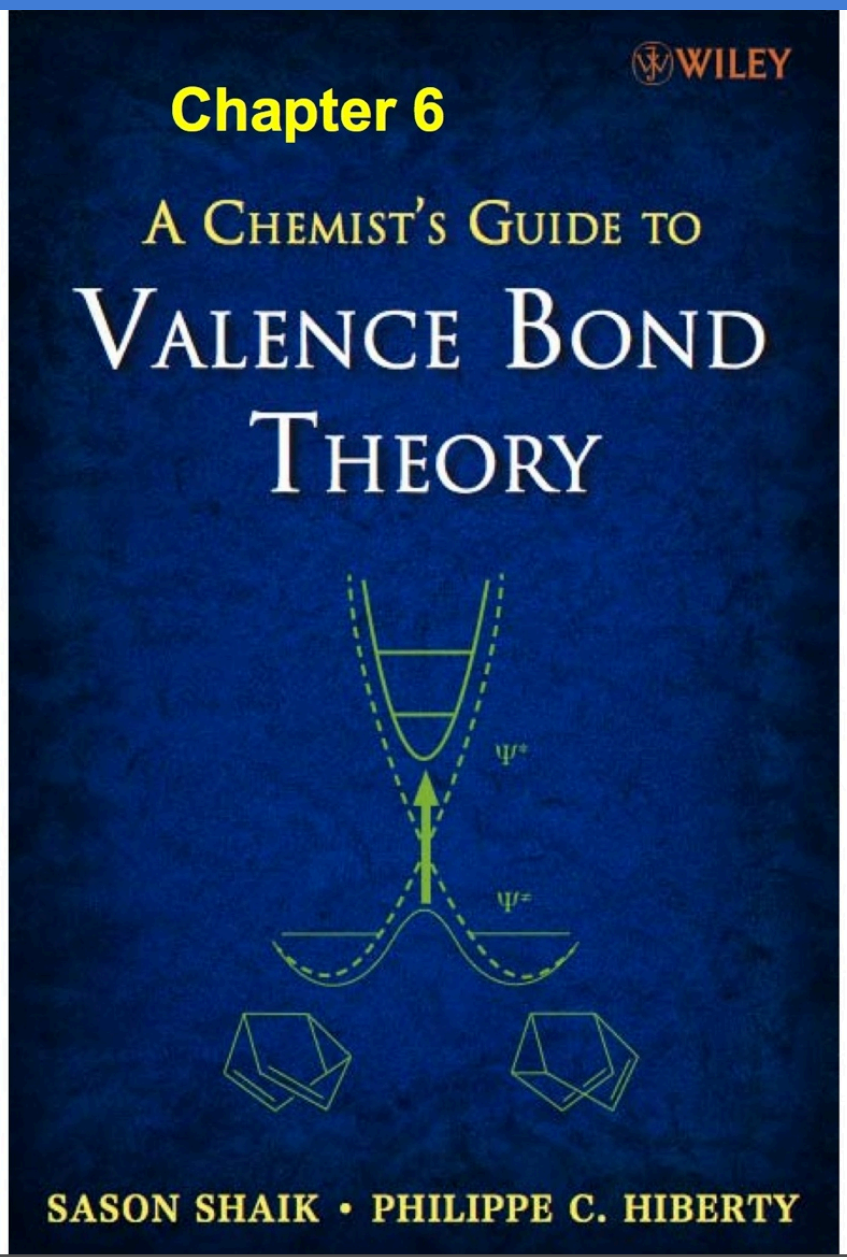


A single electron may change everything !

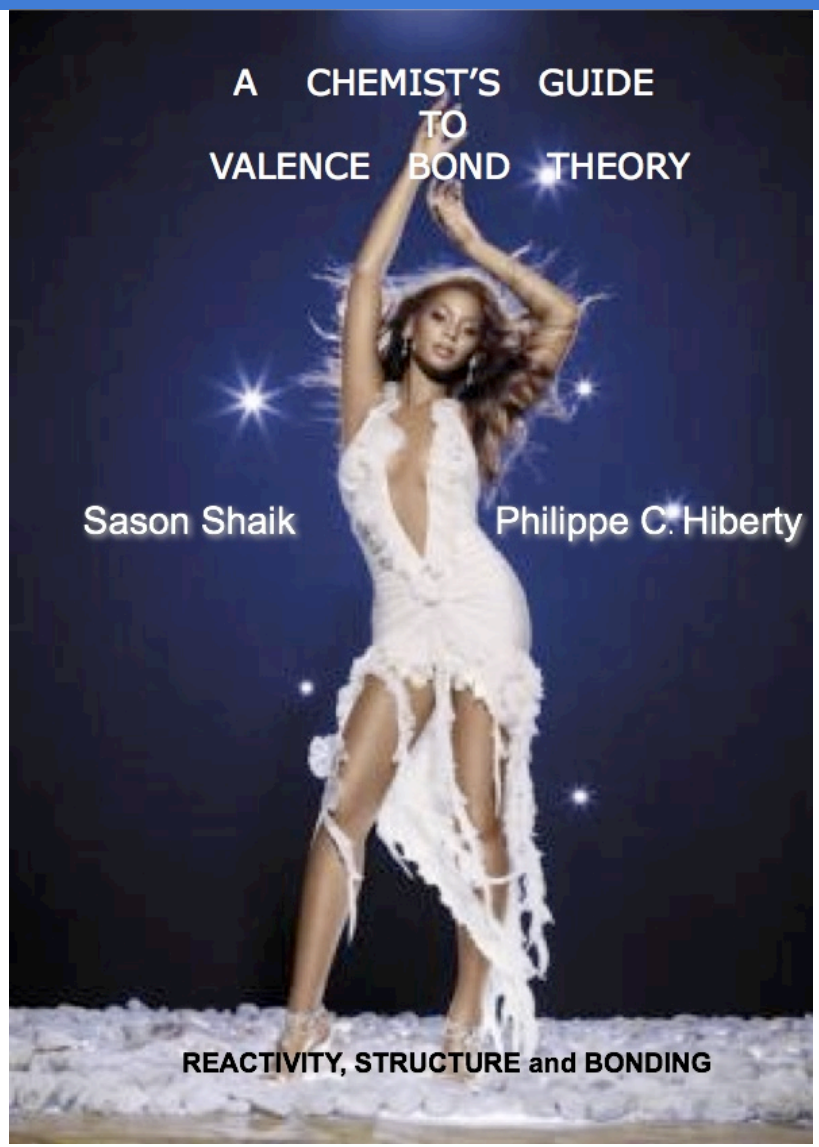
Conclusion

- A general and powerful model for reactivity :
  - Nucleophilic, electrophilic, radical, pericyclic…
  - Simple: could be applied «on the back of en envelop»
  - Insightful: allows to create order among great families of reactions
- Both interpretative and quantitative :
  - qualitative reasonings : a few rules and elementary interactions
  - quantitive proof : by high level VB calculations

To go further...



To go further...



Final conclusion